

=> file registry

FILE 'REGISTRY' ENTERED AT 15:32:42 ON 01 FEB 2008  
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STRUCTURE FILE UPDATES: 31 JAN 2008 HIGHEST RN 1001228-41-6  
 DICTIONARY FILE UPDATES: 31 JAN 2008 HIGHEST RN 1001228-41-6

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH June 29, 2007

Please note that search-term pricing does apply when  
 conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and  
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 experimental property data in the original document. For information  
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<http://www.cas.org/support/stngen/stndoc/properties.html>

=> file caplus

FILE 'CAPLUS' ENTERED AT 15:32:45 ON 01 FEB 2008  
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FILE COVERS 1907 - 1 Feb 2008 VOL 148 ISS 6  
 FILE LAST UPDATED: 31 Jan 2008 (20080131/ED)

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 They are available for your review at:

<http://www.cas.org/infopolicy.html>

'OBI' IS DEFAULT SEARCH FIELD FOR 'CAPLUS' FILE

=> d stat que L40

L2	1	SEA FILE=REGISTRY ABB=ON	PLU=ON	4635-87-4
L4	1	SEA FILE=REGISTRY ABB=ON	PLU=ON	74-90-8
L5	1	SEA FILE=REGISTRY ABB=ON	PLU=ON	106-99-0
L9	2	SEA FILE=REGISTRY ABB=ON	PLU=ON	"3-PENTENENITRILE, ("?/CN
L10	3	SEA FILE=REGISTRY ABB=ON	PLU=ON	L2 OR L9
L11	2	SEA FILE=REGISTRY ABB=ON	PLU=ON	(16529-66-1/CRN OR 16545-78-1

```

/CRN OR 4635-87-4/CRN)
L13      5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17      1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18      6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L21      17208 SEA FILE=CAPLUS ABB=ON PLU=ON L4
L22      24982 SEA FILE=CAPLUS ABB=ON PLU=ON L5
L25      130 SEA FILE=CAPLUS ABB=ON PLU=ON L18 (L) PREP/RL
L26      3070185 SEA FILE=CAPLUS ABB=ON PLU=ON (RACT OR RCT OR RGT)/RL
L27      2588 SEA FILE=CAPLUS ABB=ON PLU=ON L21 (L) L26
L28      9152 SEA FILE=CAPLUS ABB=ON PLU=ON L22 (L) L26
L29      32 SEA FILE=CAPLUS ABB=ON PLU=ON L27 AND L28 AND L25
L30      297092 SEA FILE=CAPLUS ABB=ON PLU=ON ?POROUS?/BI
L31      40403 SEA FILE=CAPLUS ABB=ON PLU=ON MICROPOR?/BI
L32      30953 SEA FILE=CAPLUS ABB=ON PLU=ON MOLECULAR SIEV?/BI
L33      128603 SEA FILE=CAPLUS ABB=ON PLU=ON ZEOLIT?/BI
L34      23369 SEA FILE=CAPLUS ABB=ON PLU=ON MESOPOR?/BI
L35      1378 SEA FILE=CAPLUS ABB=ON PLU=ON ADSORBANT?/BI
L36      375297 SEA FILE=CAPLUS ABB=ON PLU=ON CERAMIC?/BI
L40      1 SEA FILE=CAPLUS ABB=ON PLU=ON L29 AND (L30 OR L31 OR L32 OR
L33 OR L34 OR L35 OR L36)

```

=> d stat que L41

```

L2      1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10     3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
/CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18     6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L21     17208 SEA FILE=CAPLUS ABB=ON PLU=ON L4
L22     24982 SEA FILE=CAPLUS ABB=ON PLU=ON L5
L25     130 SEA FILE=CAPLUS ABB=ON PLU=ON L18 (L) PREP/RL
L26     3070185 SEA FILE=CAPLUS ABB=ON PLU=ON (RACT OR RCT OR RGT)/RL
L27     2588 SEA FILE=CAPLUS ABB=ON PLU=ON L21 (L) L26
L28     9152 SEA FILE=CAPLUS ABB=ON PLU=ON L22 (L) L26
L29     32 SEA FILE=CAPLUS ABB=ON PLU=ON L27 AND L28 AND L25
L37     54059 SEA FILE=CAPLUS ABB=ON PLU=ON AIR/CT
L38     18350 SEA FILE=CAPLUS ABB=ON PLU=ON NOBLE GAS?/BI
L39     15276 SEA FILE=CAPLUS ABB=ON PLU=ON HELIUM GROUP?/BI
L41     1 SEA FILE=CAPLUS ABB=ON PLU=ON L29 AND (L37 OR L38 OR L39)

```

=> d stat que L42

```

L2      1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10     3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
/CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18     6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17

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L21      17208 SEA FILE=CAPLUS ABB=ON  PLU=ON  L4
L22      24982 SEA FILE=CAPLUS ABB=ON  PLU=ON  L5
L23      383 SEA FILE=CAPLUS ABB=ON  PLU=ON  L18
L24      47 SEA FILE=CAPLUS ABB=ON  PLU=ON  L21 AND L22 AND L23
L30      297092 SEA FILE=CAPLUS ABB=ON  PLU=ON  ?POROUS?/BI
L31      40403 SEA FILE=CAPLUS ABB=ON  PLU=ON  MICROPOR?/BI
L32      30953 SEA FILE=CAPLUS ABB=ON  PLU=ON  MOLECULAR SIEV?/BI
L33      128603 SEA FILE=CAPLUS ABB=ON  PLU=ON  ZEOLIT?/BI
L34      23369 SEA FILE=CAPLUS ABB=ON  PLU=ON  MESOPOR?/BI
L35      1378 SEA FILE=CAPLUS ABB=ON  PLU=ON  ADSORBANT?/BI
L36      375297 SEA FILE=CAPLUS ABB=ON  PLU=ON  CERAMIC?/BI
L37      54059 SEA FILE=CAPLUS ABB=ON  PLU=ON  AIR/CT
L38      18350 SEA FILE=CAPLUS ABB=ON  PLU=ON  NOBLE GAS?/BI
L39      15276 SEA FILE=CAPLUS ABB=ON  PLU=ON  HELIUM GROUP?/BI
L42      2 SEA FILE=CAPLUS ABB=ON  PLU=ON  L24 AND (L30 OR L31 OR L32 OR
      L33 OR L34 OR L35 OR L36 OR L37 OR L38 OR L39)

```

=> d stat que L61

```

L2      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE, (?/CN
L10     3 SEA FILE=REGISTRY ABB=ON  PLU=ON  L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON  PLU=ON  (16529-66-1/CRN OR 16545-78-1
      /CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON  PLU=ON  L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE-2,2-D2"/CN

L18     6 SEA FILE=REGISTRY ABB=ON  PLU=ON  L13 OR L17
L21     17208 SEA FILE=CAPLUS ABB=ON  PLU=ON  L4
L22     24982 SEA FILE=CAPLUS ABB=ON  PLU=ON  L5
L23     383 SEA FILE=CAPLUS ABB=ON  PLU=ON  L18
L24     47 SEA FILE=CAPLUS ABB=ON  PLU=ON  L21 AND L22 AND L23
L60     1 SEA FILE=REGISTRY ABB=ON  PLU=ON  1344-28-1
L61     4 SEA FILE=CAPLUS ABB=ON  PLU=ON  L60 AND L24

```

=> d stat que L63

```

L2      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE, (?/CN
L10     3 SEA FILE=REGISTRY ABB=ON  PLU=ON  L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON  PLU=ON  (16529-66-1/CRN OR 16545-78-1
      /CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON  PLU=ON  L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE-2,2-D2"/CN

L18     6 SEA FILE=REGISTRY ABB=ON  PLU=ON  L13 OR L17
L21     17208 SEA FILE=CAPLUS ABB=ON  PLU=ON  L4
L22     24982 SEA FILE=CAPLUS ABB=ON  PLU=ON  L5
L23     383 SEA FILE=CAPLUS ABB=ON  PLU=ON  L18
L24     47 SEA FILE=CAPLUS ABB=ON  PLU=ON  L21 AND L22 AND L23
L62     314410 SEA FILE=CAPLUS ABB=ON  PLU=ON  ALUMINA/BI
L63     4 SEA FILE=CAPLUS ABB=ON  PLU=ON  L24 AND L62

```

=> d stat que L66

```

L2      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  4635-87-4

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```
L4      1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10     3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
      /CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18     6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L21     17208 SEA FILE=CAPLUS ABB=ON PLU=ON L4
L22     24982 SEA FILE=CAPLUS ABB=ON PLU=ON L5
L25     130 SEA FILE=CAPLUS ABB=ON PLU=ON L18 (L) PREP/RL
L26     3070185 SEA FILE=CAPLUS ABB=ON PLU=ON (RACT OR RCT OR RGT)/RL
L27     2588 SEA FILE=CAPLUS ABB=ON PLU=ON L21 (L) L26
L28     9152 SEA FILE=CAPLUS ABB=ON PLU=ON L22 (L) L26
L29     32 SEA FILE=CAPLUS ABB=ON PLU=ON L27 AND L28 AND L25
L64     1462878 SEA FILE=CAPLUS ABB=ON PLU=ON ?CATALY?/BI
L66     32 SEA FILE=CAPLUS ABB=ON PLU=ON L64 AND L29
```

=> d stat que L84

```
L2      1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10     3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
      /CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18     6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L21     17208 SEA FILE=CAPLUS ABB=ON PLU=ON L4
L22     24982 SEA FILE=CAPLUS ABB=ON PLU=ON L5
L23     383 SEA FILE=CAPLUS ABB=ON PLU=ON L18
L24     47 SEA FILE=CAPLUS ABB=ON PLU=ON L21 AND L22 AND L23
L76     1 SEA FILE=REGISTRY ABB=ON PLU=ON NITROGEN/CN
L77     1 SEA FILE=REGISTRY ABB=ON PLU=ON HELIUM/CN
L78     1 SEA FILE=REGISTRY ABB=ON PLU=ON ARGON/CN
L79     1 SEA FILE=REGISTRY ABB=ON PLU=ON KRYPTON/CN
L80     1 SEA FILE=REGISTRY ABB=ON PLU=ON NEON/CN
L81     1 SEA FILE=REGISTRY ABB=ON PLU=ON XENON/CN
L82     1 SEA FILE=REGISTRY ABB=ON PLU=ON RADON/CN
L83     1 SEA FILE=REGISTRY ABB=ON PLU=ON AIR/CN
L84     2 SEA FILE=CAPLUS ABB=ON PLU=ON L24 AND (L76 OR L77 OR L78 OR
      L79 OR L80 OR L81 OR L82 OR L83)
```

=> s L40 or L41 or L42 or L61 or L63 or L66 or L84

L86 34 L40 OR L41 OR L42 OR L61 OR L63 OR L66 OR L84

=> file casreact

FILE 'CASREACT' ENTERED AT 15:33:41 ON 01 FEB 2008  
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FILE CONTENT:1840 - 26 Jan 2008 VOL 148 ISS 5

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*****
*
*   CASREACT now has more than 13.8 million reactions
*
*****
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This file contains CAS Registry Numbers for easy and accurate substance identification.

```
=> d stat que L72
L2      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  4635-87-4
L9      2 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE, (?/CN
L10     3 SEA FILE=REGISTRY ABB=ON  PLU=ON  L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON  PLU=ON  (16529-66-1/CRN OR 16545-78-1
        /CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON  PLU=ON  L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE-2,2-D2"/CN

L18     6 SEA FILE=REGISTRY ABB=ON  PLU=ON  L13 OR L17
L68     39 SEA FILE=CASREACT ABB=ON  PLU=ON  L18/PRO
L69     723 SEA FILE=CASREACT ABB=ON  PLU=ON  74-90-8
L70     1995 SEA FILE=CASREACT ABB=ON  PLU=ON  106-99-0
L71     16 SEA FILE=CASREACT ABB=ON  PLU=ON  L68 (L) L69
L72     15 SEA FILE=CASREACT ABB=ON  PLU=ON  L71 (L) L70
```

```
=> file uspatfull
FILE 'USPATFULL' ENTERED AT 15:34:03 ON 01 FEB 2008
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FILE COVERS 1971 TO PATENT PUBLICATION DATE: 31 Jan 2008 (20080131/PD)  
FILE LAST UPDATED: 31 Jan 2008 (20080131/ED)  
HIGHEST GRANTED PATENT NUMBER: US7325253  
HIGHEST APPLICATION PUBLICATION NUMBER: US2008028492  
CA INDEXING IS CURRENT THROUGH 31 Jan 2008 (20080131/UPCA)  
ISSUE CLASS FIELDS (/INCL) CURRENT THROUGH: 31 Jan 2008 (20080131/PD)  
REVISED CLASS FIELDS (/NCL) LAST RELOADED: Dec 2007  
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Dec 2007

```
=> d stat que L44
L2      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE, (?/CN
L10     3 SEA FILE=REGISTRY ABB=ON  PLU=ON  L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON  PLU=ON  (16529-66-1/CRN OR 16545-78-1
        /CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON  PLU=ON  L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE-2,2-D2"/CN
```

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L18      6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L30      297092 SEA FILE=CAPLUS ABB=ON PLU=ON ?POROUS?/BI
L31      40403 SEA FILE=CAPLUS ABB=ON PLU=ON MICROPOR?/BI
L32      30953 SEA FILE=CAPLUS ABB=ON PLU=ON MOLECULAR SIEV?/BI
L33      128603 SEA FILE=CAPLUS ABB=ON PLU=ON ZEOLIT?/BI
L34      23369 SEA FILE=CAPLUS ABB=ON PLU=ON MESOPOR?/BI
L35      1378 SEA FILE=CAPLUS ABB=ON PLU=ON ADSORBANT?/BI
L36      375297 SEA FILE=CAPLUS ABB=ON PLU=ON CERAMIC?/BI
L43      24 SEA FILE=USPATFULL ABB=ON PLU=ON L4 AND L5 AND L18
L44      6 SEA FILE=USPATFULL ABB=ON PLU=ON L43 AND (L30 OR L31 OR L32
OR L33 OR L34 OR L35 OR L36)

```

=> d stat que L45

```

L2      1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10     3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
/CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18      6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L37      54059 SEA FILE=CAPLUS ABB=ON PLU=ON AIR/CT
L38      18350 SEA FILE=CAPLUS ABB=ON PLU=ON NOBLE GAS?/BI
L39      15276 SEA FILE=CAPLUS ABB=ON PLU=ON HELIUM GROUP?/BI
L43      24 SEA FILE=USPATFULL ABB=ON PLU=ON L4 AND L5 AND L18
L45      2 SEA FILE=USPATFULL ABB=ON PLU=ON L43 AND (L37 OR L38 OR L39)

```

=> d stat que L48

```

L2      1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10     3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
/CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18      6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L43      24 SEA FILE=USPATFULL ABB=ON PLU=ON L4 AND L5 AND L18
L47      250630 SEA FILE=USPATFULL ABB=ON PLU=ON HELIUM OR ARGON OR NEON OR
KRYPTON OR XENON OR RADON
L48      14 SEA FILE=USPATFULL ABB=ON PLU=ON L47 AND L43

```

=> d stat que L51

```

L2      1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10     3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
/CRN OR 4635-87-4/CRN)

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```
L13      5 SEA FILE=REGISTRY ABB=ON  PLU=ON  L10 OR L11
L17      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE-2,2-D2"/CN

L18      6 SEA FILE=REGISTRY ABB=ON  PLU=ON  L13 OR L17
L43      24 SEA FILE=USPATFULL ABB=ON  PLU=ON  L4 AND L5 AND L18
L50     1664593 SEA FILE=USPATFULL ABB=ON  PLU=ON  AIR OR NITROGEN
L51      15 SEA FILE=USPATFULL ABB=ON  PLU=ON  L43 AND L50

=> d stat que L57
L2       1 SEA FILE=REGISTRY ABB=ON  PLU=ON  4635-87-4
L4       1 SEA FILE=REGISTRY ABB=ON  PLU=ON  74-90-8
L5       1 SEA FILE=REGISTRY ABB=ON  PLU=ON  106-99-0
L9       2 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE, (")?/CN
L10      3 SEA FILE=REGISTRY ABB=ON  PLU=ON  L2 OR L9
L11      2 SEA FILE=REGISTRY ABB=ON  PLU=ON  (16529-66-1/CRN OR 16545-78-1
        /CRN OR 4635-87-4/CRN)
L13      5 SEA FILE=REGISTRY ABB=ON  PLU=ON  L10 OR L11
L17      1 SEA FILE=REGISTRY ABB=ON  PLU=ON  "3-PENTENENITRILE-2,2-D2"/CN

L18      6 SEA FILE=REGISTRY ABB=ON  PLU=ON  L13 OR L17
L25     130 SEA FILE=CAPLUS ABB=ON  PLU=ON  L18 (L) PREP/RL
L43      24 SEA FILE=USPATFULL ABB=ON  PLU=ON  L4 AND L5 AND L18
L53     485246 SEA FILE=USPATFULL ABB=ON  PLU=ON  CATALY?
L54      24 SEA FILE=USPATFULL ABB=ON  PLU=ON  L43 AND L53
L55      TRANSFER PLU=ON L25 1- PN : 646 TERMS
L56     56 SEA FILE=USPATFULL ABB=ON  PLU=ON  L55
L57      18 SEA FILE=USPATFULL ABB=ON  PLU=ON  L56 AND L54

=> s L44 or L45 or L48 or L51 or L57
L87     24 L44 OR L45 OR L48 OR L51 OR L57

=> file stnguide
FILE 'STNGUIDE' ENTERED AT 15:35:01 ON 01 FEB 2008
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FILE CONTAINS CURRENT INFORMATION.
LAST RELOADED: Jan 25, 2008 (20080125/UP).

=> dup rem L86 L72 L87
FILE 'CAPLUS' ENTERED AT 15:35:24 ON 01 FEB 2008
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2008 AMERICAN CHEMICAL SOCIETY (ACS)

FILE 'CASREACT' ENTERED AT 15:35:24 ON 01 FEB 2008
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FILE 'USPATFULL' ENTERED AT 15:35:24 ON 01 FEB 2008
CA INDEXING COPYRIGHT (C) 2008 AMERICAN CHEMICAL SOCIETY (ACS)
PROCESSING COMPLETED FOR L86
PROCESSING COMPLETED FOR L72
PROCESSING COMPLETED FOR L87
L88      60 DUP REM L86 L72 L87 (13 DUPLICATES REMOVED)
        ANSWERS '1-34' FROM FILE CAPLUS
        ANSWERS '35-37' FROM FILE CASREACT
        ANSWERS '38-60' FROM FILE USPATFULL
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=> d ibib abs hitind hitstr L88 1-34; d ibib abs hit L88 35-37; d ibib abs kwic hit hitstr L88 38-60

L88 ANSWER 1 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 1  
 ACCESSION NUMBER: 2005:729622 CAPLUS Full-text  
 DOCUMENT NUMBER: 143:195585  
 TITLE: Catalytic hydrocyanation production of  
 3-pentenitrile from 1,3-butadiene and hydrogen  
 cyanide  
 INVENTOR(S): Scheidel, Jens; Jungkamp, Tim; Bartsch, Michael;  
 Haderlein, Gerd; Baumann, Robert; Luyken, Hermann  
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany  
 SOURCE: PCT Int. Appl., 48 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073175	A1	20050811	WO 2005-EP784	20050127
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
DE 102004004724	A1	20050818	DE 2004-102004004724	20040129
CA 2552862	A1	20050811	CA 2005-2552862	20050127
EP 1716106	A1	20061102	EP 2005-707030	20050127
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS			
CN 1914161	A	20070214	CN 2005-80003699	20050127
BR 2005007129	A	20070619	BR 2005-7129	20050127
JP 2007519677	T	20070719	JP 2006-550103	20050127
MX 2006PA07886	A	20061002	MX 2006-PA7886	20060710
KR 2007011277	A	20070124	KR 2006-715314	20060728
IN 2006CN03125	A	20070608	IN 2006-CN3125	20060829
PRIORITY APPLN. INFO.:			DE 2004-102004004724A	20040129
			WO 2005-EP784	W 20050127

OTHER SOURCE(S): CASREACT 143:195585

AB A method is described for producing 3-pentenitrile by means of the hydrocyanation of 1,3-butadiene, where 1,3-butadiene is reacted with hydrogen cyanide in the presence of at least one Ni-phosphorus ligand complex catalyst, and the resulting flow is purified by distillation, the bottom temperature not exceeding 140° during the distillation. Process flow diagrams are presented.

IC ICM C07C253-10  
 ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
 Section cross-reference(s): 23, 48, 67

ST pentenenitrile manuf catalytic hydrocyanation butadiene distn

IT Alkadienes  
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical

process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)  
 (1,3-butadiene; catalytic hydrocyanation production of  
 3-pentenitrile from 1,3-butadiene and hydrogen cyanide)

IT Hydrocyanation catalysts  
 (Ni-phosphorus ligand complexes; catalytic hydrocyanation  
 production of 3-pentenitrile from 1,3-butadiene and hydrogen cyanide)

IT Hydrocyanation  
 (catalytic hydrocyanation production of 3-pentenitrile from  
 1,3-butadiene and hydrogen cyanide)

IT Distillation  
 Distillation apparatus  
 Distillation columns  
 (in the catalytic hydrocyanation production of 3-pentenitrile  
 from 1,3-butadiene and hydrogen cyanide)

IT Phosphites  
 RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical,  
 engineering or chemical process); PROC (Process); USES (Uses)  
 (ligands; in the catalytic hydrocyanation production of  
 3-pentenitrile from 1,3-butadiene and hydrogen cyanide)

IT Nitriles, preparation  
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
 (Physical, engineering or chemical process); PREP (Preparation); PROC  
 (Process)  
 (unsatd., 3-pentenitriles; catalytic hydrocyanation production  
 of 3-pentenitrile from 1,3-butadiene and hydrogen cyanide)

IT 4635-87-4P, 3-Pentenitrile  
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
 (Physical, engineering or chemical process); PREP (Preparation);  
 PROC (Process)  
 (catalytic hydrocyanation production of 3-pentenitrile from  
 1,3-butadiene and hydrogen cyanide)

IT 590-18-1, cis-2-Butene  
 RL: EPR (Engineering process); NUU (Other use, unclassified); PEP  
 (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
 (catalytic hydrocyanation production of 3-pentenitrile from  
 1,3-butadiene and hydrogen cyanide)

IT 74-90-8, Hydrogen cyanide, reactions 196-99-0,  
 1,3-Butadiene, reactions 16529-66-1, trans-3-Pentenitrile  
 16545-78-1, cis-3-Pentenitrile  
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical  
 process); RCT (Reactant); PROC (Process); RACT (Reactant or  
 reagent)  
 (catalytic hydrocyanation production of 3-pentenitrile from  
 1,3-butadiene and hydrogen cyanide)

IT 1295-35-8 220472-84-4 509083-87-8  
 RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical,  
 engineering or chemical process); PROC (Process); USES (Uses)  
 (ligand; catalytic hydrocyanation production of 3-pentenitrile  
 from 1,3-butadiene and hydrogen cyanide)

IT 4635-87-4P, 3-Pentenitrile  
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
 (Physical, engineering or chemical process); PREP (Preparation);  
 PROC (Process)  
 (catalytic hydrocyanation production of 3-pentenitrile from  
 1,3-butadiene and hydrogen cyanide)

RN 4635-87-4 CAPLUS

CN 3-Pentenitrile (CA INDEX NAME)

10/586490



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: EPR (Engineering process); PEP (Physical, engineering or chemical  
process); RCT (Reactant); PROC (Process); RACT (Reactant or  
reagent)  
(catalytic hydrocyanation production of 3-pentenitrile from  
1,3-butadiene and hydrogen cyanide)  
RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 2 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 2  
ACCESSION NUMBER: 2005:729621 CAPLUS Full-text  
DOCUMENT NUMBER: 143:195584  
TITLE: Manufacture of linear 3-pentenitrile from streams  
containing 2-methyl-3-butenitrile  
INVENTOR(S): Jungkamp, Tim; Baumann, Robert; Bartsch, Michael;  
Haderlein, Gerd; Luyken, Hermann; Scheidel, Jens;  
Aechtner, Tobias; Pfab, Peter; Deckert, Petra  
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany  
SOURCE: PCT Int. Appl., 116 pp.  
CODEN: PIXXD2  
DOCUMENT TYPE: Patent  
LANGUAGE: German  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073174	A1	20050811	WO 2005-EP781	20050127
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				

RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,  
 AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,  
 EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT,  
 RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,  
 MR, NE, SN, TD, TG

DE 102004004671	A1	20050818	DE 2004-102004004671	20040129
DE 102004042949	A1	20060309	DE 2004-102004042949	20040902
DE 102004063381	A1	20060706	DE 2004-102004063381	20041223
CA 2554736	A1	20050811	CA 2005-2554736	20050127
EP 1716105	A1	20061102	EP 2005-707029	20050127
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS				
CN 1914159	A	20070214	CN 2005-80003693	20050127
BR 2005007197	A	20070626	BR 2005-7197	20050127
JP 2007519675	T	20070719	JP 2006-550101	20050127
MX 2006PA07813	A	20060926	MX 2006-PA7813	20060707
IN 2006CN03134	A	20070608	IN 2006-CN3134	20060829

## PRIORITY APPLN. INFO.:

DE 2004-102004004671A	20040129
DE 2004-102004042949A	20040902
DE 2004-102004063381A	20041223
WO 2005-EP781	W 20050127

OTHER SOURCE(S): CASREACT 143:195584; MARPAT 143:195584

AB The title compound, an adiponitrile intermediate useful for the manufacture of polyamides, is manufactured by (A) isomerization of an educt stream containing 2-methyl-3-butenenitrile obtained by hydrocyanation of 1,3-butadiene on  $\geq 1$  dissolved or dispersed isomerization catalyst to form a stream (1), which contains the isomerization catalyst(s), 2-methyl-3-butenenitrile, 3-pentenitrile and (Z)-2-methyl-2-butenenitrile; (B) distillation of the stream (1) to obtain a stream (2) as the overhead product, which contains 2-methyl-3-butenenitrile, 3-pentenitrile and (Z)-2-methyl-2-butenenitrile and a stream (3) as the bottom product, which contains the isomerization catalyst(s); (C) distillation of the stream (2) to obtain a stream (4) as the overhead product, which is enriched with (Z)-2-methyl-2-butenenitrile in comparison to stream (2), [in relation to the sum of all pentenenitriles in stream (2)] and a stream (5) as the bottom product, which is enriched with 3-pentenitrile and 2-methyl-3-butenenitrile in comparison to stream (2), [in relation to the sum of all pentenenitriles in stream (2)]; (D) distillation of stream (5) to obtain a stream (6) as the bottom product, which contains 3-pentenitrile and a stream (7) as the head product, which contains 2-methyl-3-butenenitrile. The process is exemplified by use of block schematic diagrams.

IC ICM C07C253-10

ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

IT Distillation

Hydrocyanation catalysts

Isomerization

(manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT Isomerization catalysts

(nickel compds. with o-isopropylphenyl-m/p-tolyl phosphites; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 7440-02-0D, Nickel, compds. with P-containing ligands 25586-42-9D, Tritolyl phosphite, nickel complexes 509083-87-8D, nickel complexes 861509-78-6D, nickel complexes

RL: CAT (Catalyst use); USES (Uses)

(hydrocyanation catalysts; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 74-90-3, Hydrogen cyanide, reactions

RL: PCT (Reactant); PACT (Reactant or reagent)

10/586490

(hydrocyanation of butadiene; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 106-99-0, 1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 4635-87-4E, 3-Pentenenitrile  
RL: IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PYP (Physical process); PREP (Preparation); PROC (Process)  
(manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 74-90-8, Hydrogen cyanide, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation of butadiene; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, 1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4E, 3-Pentenenitrile  
RL: IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PYP (Physical process); PREP (Preparation); PROC (Process)  
(manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

RN 4635-87-4 CAPLUS

CN 3-Pentenenitrile (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT



10/586490

L88 ANSWER 3 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 3

ACCESSION NUMBER: 2005:729620 CAPLUS Full-text

DOCUMENT NUMBER: 143:195583

TITLE: Method for the hydrocyanation of 1,3-butadiene into 3-pentenitrile using a loop-type bubble column reactor comprising an external pumping circuit and a jet nozzle for driving the inner circulation

INVENTOR(S): Jungkamp, Tim; Baumann, Robert; Bartsch, Michael; Haderlein, Gerd; Luyken, Hermann; Scheidel, Jens

PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany

SOURCE: PCT Int. Appl., 24 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073173	A1	20050811	WO 2005-EP780	20050127
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
DE 102004004673	A1	20050818	DE 2004-102004004673	20040129
EP 1713762	A1	20061025	EP 2005-707028	20050127
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS			
CN 1914155	A	20070214	CN 2005-80003622	20050127
JP 2007519674	T	20070719	JP 2006-550100	20050127
PRIORITY APPLN. INFO.:			DE 2004-102004004673A	20040129
			WO 2005-EP780	W 20050127

OTHER SOURCE(S): CASREACT 143:195583

AB A method for producing 3-pentenitrile by means of the hydrocyanation of 1,3-butadiene in the presence of at least one catalyst is described where the hydrocyanation reaction is carried out in a loop-type bubble reactor column comprising an external pumping circuit and a jet nozzle for driving the inner circulation.

IC ICM C07C253-10

ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 48

ST pentenenitrile manuf catalytic hydrocyanation butadiene loop type reactor

IT Hydrocyanation

Hydrocyanation catalysts

(method for the hydrocyanation of 1,3-butadiene into 3-pentenitrile using a loop-type bubble column reactor comprising an external pumping circuit and a jet nozzle for driving the inner circulation)

IT 4635-87-4E, 3-Pentenitrile

RL: IMF (Industrial manufacture); FSEP (Preparation)

(method for the hydrocyanation of 1,3-butadiene into 3-pentenitrile using a loop-type bubble column reactor comprising an external pumping circuit and a jet nozzle for driving the inner circulation)

10/586490

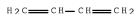
IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: PCT (Reactant); PACT (Reactant or reagent)  
(method for the hydrocyanation of 1,3-butadiene into 3-pentenitrile  
using a loop-type bubble column reactor comprising an external pumping  
circuit and a jet nozzle for driving the inner circulation)  
IT 4635-87-4E, 3-Pentenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(method for the hydrocyanation of 1,3-butadiene into 3-pentenitrile  
using a loop-type bubble column reactor comprising an external pumping  
circuit and a jet nozzle for driving the inner circulation)  
RN 4635-87-4 CAPLUS  
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(method for the hydrocyanation of 1,3-butadiene into 3-pentenitrile  
using a loop-type bubble column reactor comprising an external pumping  
circuit and a jet nozzle for driving the inner circulation)  
RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L98 ANSWER 4 OF 60 CAPLUS COPYRIGHT 2009 ACS on STN DUPLICATE 4  
ACCESSION NUMBER: 2005:729618 CAPLUS Full-text  
DOCUMENT NUMBER: 143:195581  
TITLE: Catalytic hydrocyanation method for producing  
3-pentenitrile from hydrogen cyanide and  
1,3-butadiene  
INVENTOR(S): Scheidel, Jens; Jungkamp, Tim; Bartsch, Michael;  
Haderlein, Gerd; Baumann, Robert; Luyken, Hermann  
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany  
SOURCE: PCT Int. Appl., 55 pp.  
CODEN: PIXXD2

DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073171	A1	20050811	WO 2005-EP774	20050127
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
DE 102004004720	A1	20050818	DE 2004-102004004720	20040129
CA 2552860	A1	20050811	CA 2005-2552860	20050127
EP 1716104	A1	20061102	EP 2005-701203	20050127
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS				
CN 1914154	A	20070214	CN 2005-80003621	20050127
BR 2005006587	A	20070502	BR 2005-6587	20050127
JP 2007519672	T	20070719	JP 2006-550097	20050127
MX 2006PA07883	A	20061002	MX 2006-PA7883	20060710
KR 2007011278	A	20070124	KR 2006-715315	20060728
IN 2006CN03123	A	20070608	IN 2006-CN3123	20060829
PRIORITY APPLN. INFO.:			DE 2004-102004004720A	20040129
			WO 2005-EP774	W 20050127

OTHER SOURCE(S): CASREACT 143:195581

AB A method is described for producing 3-pentenitrile comprising: (a) 1,3-butadiene is reacted with hydrogen cyanide over at least one catalyst to obtain a flow (1) containing 3-pentenitrile, 2-methyl-3-butenitrile, the catalyst, and 1,3-butadiene; (b) the flow (1) is distilled in a column to obtain a head product flow (2) rich in 1,3-butadiene, and a bottom product flow (3) that is poor in 1,3-butadiene and contains 3-pentenitrile, the catalyst, and 2-methyl-3-butenitrile; (c) the flow (3) is distilled in a column to obtain a head product flow (4) containing 1,3-butadiene, a flow (5) in a side-tap of the column, containing 3-pentenitrile and 2-methyl-3-butenitrile, and a bottom product flow (6) containing the catalyst; and (d) the flow (5) is distilled to obtain a head product flow (7) containing 2-methyl-3-butenitrile and a bottom product flow (8) containing 3-pentenitrile. Process flow diagrams are presented.

IC ICM C07C253-10

ICS C07C253-34; C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 48, 67

ST pentenenitrile manuf catalytic hydrocyanation butadiene

IT Alkadienes

RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent) (1,3-butadiene; catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)

IT Hydrocyanation

(catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)

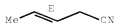
IT Hydrocyanation catalysts

- (elemental Ni-phosphine complexes; catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT Distillation  
Distillation apparatus  
Distillation columns  
Isomerization  
Isomerization catalysts  
Process control  
(in a catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT Phosphines  
Phosphites  
Phosphonates  
RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(ligands; in a catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT Nitriles, preparation  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PREP (Preparation); PROC (Process)  
(unsatd., 3-pentenitriles; catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 592-51-8P, 4-Pentenitrile 26294-98-4P, trans-2-Pentenitrile  
RL: BYP (Byproduct); EPR (Engineering process); PEP (Physical, engineering or chemical process); PREP (Preparation); PROC (Process)  
(catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 7440-02-0, Nickel, uses  
RL: CAT (Catalyst use); USES (Uses)  
(catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 220472-84-4 509083-87-8  
RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 16529-66-1P 16545-78-1P, cis-3-Pentenitrile  
25899-50-7P, cis-2-Pentenitrile  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PREP (Preparation); PROC (Process)  
(catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 4635-87-4E, 3-Pentenitrile  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PYP (Physical process); PREP (Preparation); PROC (Process)  
(catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 16529-56-9P, 2-Methyl-3-butenitrile  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PYP (Physical process); RCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)  
(catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions  
RL: EPR (Engineering process); PEP (Physical, engineering or chemical

10/586490

process); PYP (Physical process); RCT (Reactant); PROC  
(Process); RACT (Reactant or reagent)  
(catalytic hydrocyanation method for producing  
3-pentenitrile from hydrogen cyanide and 1,3-butadiene)  
IT 16529-66-1P 16545-78-1P, cis-3-Pentenitrile  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
(Physical, engineering or chemical process); PUR (Purification or  
recovery); PREP (Preparation); PROC (Process)  
(catalytic hydrocyanation method for producing  
3-pentenitrile from hydrogen cyanide and 1,3-butadiene)  
RN 16529-66-1 CAPLUS  
CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 CAPLUS  
CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.

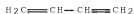


IT 4635-87-4P, 3-Pentenitrile  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
(Physical, engineering or chemical process); PYP (Physical process);  
PREP (Preparation); PROC (Process)  
(catalytic hydrocyanation method for producing  
3-pentenitrile from hydrogen cyanide and 1,3-butadiene)  
RN 4635-87-4 CAPLUS  
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-6, Hydrogen cyanide, reactions 166-99-0,  
1,3-Butadiene, reactions  
RL: EPR (Engineering process); PEP (Physical, engineering or chemical  
process); PYP (Physical process); RCT (Reactant); PROC  
(Process); RACT (Reactant or reagent)  
(catalytic hydrocyanation method for producing  
3-pentenitrile from hydrogen cyanide and 1,3-butadiene)  
RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)

RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 5 OF 60 CAPLUS COPYRIGHT 2008 ACS on SIN DUPLICATE 5  
ACCESSION NUMBER: 2005:729617 CAPLUS Full-text  
DOCUMENT NUMBER: 143:195580  
TITLE: Continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide  
INVENTOR(S): Bartsch, Michael; Baumann, Robert; Haderlein, Gerd; Scheidel, Jens; Jungkamp, Tim; Luyken, Hermann  
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany  
SOURCE: PCT Int. Appl., 31 pp.  
CODEN: PIXXD2  
DOCUMENT TYPE: Patent  
LANGUAGE: German  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073170	A1	20050811	WO 2005-EP772	20050127
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
DE 102004004696	A1	20050818	DE 2004-102004004696	20040129
CA 2553027	A1	20050811	CA 2005-2553027	20050127
EP 1716103	A1	20061102	EP 2005-701201	20050127
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS				
CN 1914157	A	20070214	CN 2005-80003675	20050127
BR 2005007193	A	20070626	BR 2005-7193	20050127
JP 2007519671	T	20070719	JP 2006-550095	20050127
MX 2006PA07882	A	20061002	MX 2006-PA7882	20060710
IN 2006CN03128	A	20070608	IN 2006-CN3128	20060829
PRIORITY APPLN. INFO.:			DE 2004-102004004696A	20040129
			WO 2005-EP772	W 20050127

OTHER SOURCE(S): CASREACT 143:195580

AB A method for continuous hydrocyanation of 1,3-butadiene into linear pentenenitriles in the presence of at least one elemental nickel catalyst with chelate ligands, where 1,3-butadiene and HCN are used in a molar ratio of 1.1-1.6:1, resp.

IC ICM C07C253-10  
ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 48, 67

ST pentenenitrile manuf butadiene catalytic hydrocyanation

IT Alkadienes  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(1,3-butadiene; continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT Lewis acids  
RL: CAT (Catalyst use); USES (Uses)  
(catalysts; continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT Distillation  
Process control  
(in a continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT Phosphines  
Phosphites  
Phosphonates  
RL: CAT (Catalyst use); USES (Uses)  
(ligands; continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT Nitriles, preparation  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(unsatd., linear pentenenitriles; continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT 16529-56-9P, 2-Methyl-3-butenitrile  
RL: BYP (Byproduct); PREP (Preparation)  
(continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT 1295-35-8, Bis(cyclooctadienyl)nickel 7440-02-0, Nickel, uses 7646-85-7, Zinc chloride, uses 220472-84-4 509083-87-8 509095-18-5 851024-54-9  
RL: CAT (Catalyst use); USES (Uses)  
(continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT 4635-87-4E, 3-Pentenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT 4635-87-4E, 3-Pentenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

10/586490

RN 4635-87-4 CAPLUS  
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(continuous catalytic hydrocyanation method for the production of  
linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)  
RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 6 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 6

ACCESSION NUMBER: 2005:729616 CAPLUS [Full-text](#)

DOCUMENT NUMBER: 143:195579

TITLE: Process control in a catalytic hydrocyanation method  
for the conversion of 1,3-butadiene and hydrogen  
cyanide into 3-pentenitrile

INVENTOR(S): Jungkamp, Tim; Baumann, Robert; Schroeder, Thorsten;  
Bartsch, Michael; Haderlein, Gerd; Luyken, Hermann;  
Scheidel, Jens

PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany

SOURCE: PCT Int. Appl., 28 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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WO 2005073169	A1	20050811	WO 2005-EP725	20050126
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,				



LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI,  
 NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY,  
 TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW  
 RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,  
 AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,  
 EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT,  
 RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,  
 MR, NE, SN, TD, TG

DE 102004004672 A1 20050818 DE 2004-102004004672 20040129  
 CA 2553241 A1 20050811 CA 2005-2553241 20050126  
 EP 1716107 A1 20061102 EP 2005-715210 20050126

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,  
 IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS

CN 1914156 A 20070214 CN 2005-80003641 20050126  
 BR 2005006574 A 20070410 BR 2005-6574 20050126  
 JP 2007519666 T 20070719 JP 2006-550082 20050126  
 MX 2006PA08046 A 20061019 MX 2006-PA08046 20060714  
 KR 2007011283 A 20070124 KR 2006-715350 20060728  
 IN 2006CN03130 A 20070608 IN 2006-CN3130 20060829

PRIORITY APPLN. INFO.:

DE 2004-102004004672A 20040129  
 WO 2005-EP725 W 20050126

OTHER SOURCE(S): CASREACT 143:195579

AB A method is described for the production of 3-pentenitrile by the  
 hydrocyanation of 1,3-butadiene in the presence of at least one catalyst,  
 where the 1,3-butadiene which has not been hydrocyanated is removed from the  
 product from the hydrocyanation reaction and recycled into the initial  
 hydrocyanation process and the recycled 1,3-butadiene is monitored (e.g.,  
 liquid-phase IR spectroscopy) for hydrogen cyanide content.

IC ICM C07C253-10  
 ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
 Section cross-reference(s): 23, 48

ST pentenenitrile manuf catalytic hydrocyanation butadiene hydrogen cyanide  
 process control

IT Alkadienes

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (1,3-butadiene; process control in a catalytic hydrocyanation  
 method for the conversion of 1,3-butadiene and hydrogen cyanide into  
 3-pentenitrile)

IT Phosphines  
 Phosphites  
 Phosphonates

RL: CAT (Catalyst use); USES (Uses)  
 (ligands; process control in a catalytic hydrocyanation  
 method for the conversion of 1,3-butadiene and hydrogen cyanide into  
 3-pentenitrile using)

IT Hydrocyanation

Hydrocyanation catalysts

Process control

(process control in a catalytic hydrocyanation method for the  
 conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenitrile)

IT Density

Dielectric constant

Gas chromatography

Heat capacity

IR spectroscopy

(process control in a catalytic hydrocyanation method for the  
 conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenitrile  
 using)

IT Nitriles, preparation

RL: IMF (Industrial manufacture); PREP (Preparation)  
 (unsatd., 3-pentenitrile; process control in a catalytic  
 hydrocyanation method for the conversion of 1,3-butadiene and hydrogen  
 cyanide into 3-pentenitrile)

IT 4635-87-4P, 3-Pentenitrile  
 RL: IMF (Industrial manufacture); PREP (Preparation)  
 (process control in a catalytic hydrocyanation method for the  
 conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenitrile)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (process control in a catalytic hydrocyanation method for the  
 conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenitrile)

IT 4635-87-4P, 3-Pentenitrile  
 RL: IMF (Industrial manufacture); PREP (Preparation)  
 (process control in a catalytic hydrocyanation method for the  
 conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenitrile)

RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (process control in a catalytic hydrocyanation method for the  
 conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenitrile)

RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS  
 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 7 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 7  
 ACCESSION NUMBER: 2005:729615 CAPLUS [Full-text](#)  
 DOCUMENT NUMBER: 143:195578  
 TITLE: Catalytic hydrocyanation of 1,3-butadiene with  
 hydrogen cyanide in the presence of at least one  
 microporous solid for the manufacture of

INVENTOR(S): 3-pentenitrile  
Jungkamp, Tim; Kunsmann-Keitel, Dagmar Pascale;  
Bartsch, Michael; Baumann, Robert; Haderlein, Gerd;  
Luyken, Hermann; Scheidel, Jens  
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany  
SOURCE: PCT Int. Appl., 24 pp.  
CODEN: PIXXD2  
DOCUMENT TYPE: Patent  
LANGUAGE: German  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073168	A1	20050811	WO 2005-EP723	20050126
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
DE 102004004684	A1	20050818	DE 2004-102004004684	20040129
CA 2560096	A1	20050811	CA 2005-2560096	20050126
EP 1713761	A1	20061025	EP 2005-707006	20050126
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS			
CN 1914158	A	20070214	CN 2005-80003677	20050126
BR 2005007199	A	20070626	BR 2005-7199	20050126
JP 2007519664	T	20070719	JP 2006-550080	20050126
MX 2006PA07750	A	20060926	MX 2006-PA7750	20060706
US 2007155977	A1	20070705	US 2006-586490	20060720
IN 2006CN03126	A	20070608	IN 2006-CN3126	20060829
PRIORITY APPLN. INFO.:			DE 2004-102004004684A	20040129
			WO 2005-EP723	W 20050126

OTHER SOURCE(S): CASREACT 143:195578

AB A method for the production of 3-pentenitrile is described which comprises the hydrocyanation of 1,3-butadiene with HCN over at least one catalyst, where the 1,3-butadiene and/or HCN is brought into contact with at least one microporous solid (e.g., 4A mol. sieves) prior to the reaction.

IC ICM C07C253-10

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 48

ST catalytic hydrocyanation butadiene manuf pentenenitrile microporous solid usage

IT Alkadienes  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(1,3-butadiene; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)

IT Hydrocyanation  
Hydrocyanation Catalysts  
Molecular sieves  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)

- IT Air  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile using)
- IT Noble gases, uses  
RL: NUU (Other use, unclassified); USES (Uses)  
(gases; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile using)
- IT Porous materials  
(microporous; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT Drying  
(of microporous solid; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT Nitriles, preparation  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(unsatd., 3-pentenitrile; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT 16529-56-9P, 2-Methyl-3-butenitrile  
RL: BYP (Byproduct); PREP (Preparation)  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT 4635-87-4P, 3-Pentenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT 7727-37-9, Nitrogen, uses  
RL: NUU (Other use, unclassified); USES (Uses)  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile using)
- IT 74-86-2, Acetylene, uses  
RL: NUU (Other use, unclassified); USES (Uses)  
(feed impurity; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT 1344-28-1, Alumina, processes  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PYP (Physical process); PROC (Process); USES (Uses)  
(microporous solid; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT 4635-87-4P, 3-Pentenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- RN 4635-87-4 CAPLUS

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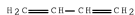
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen  
cyanide in the presence of at least one microporous solid for  
the manufacture of 3-pentenitrile)  
RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



IT 7727-37-9, Nitrogen, uses  
RL: NUU (Other use, unclassified); USES (Uses)  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen  
cyanide in the presence of at least one microporous solid for  
the manufacture of 3-pentenitrile using)  
RN 7727-37-9 CAPLUS  
CN Nitrogen (CA INDEX NAME)



IT 1344-28-1, Alumina, processes  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical  
process); PYP (Physical process); PROC (Process); USES (Uses)  
(microporous solid; catalytic hydrocyanation of  
1,3-butadiene with hydrogen cyanide in the presence of at least one  
microporous solid for the manufacture of 3-pentenitrile)  
RN 1344-28-1 CAPLUS  
CN Aluminum oxide (Al2O3) (CA INDEX NAME)

\*\*\* STRUCTURE DIAGRAM IS NOT AVAILABLE \*\*\*  
REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

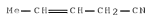
L88 ANSWER 8 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 8  
 ACCESSION NUMBER: 2005:729614 CAPLUS Full-text  
 DOCUMENT NUMBER: 143:195577  
 TITLE: Method for the production of adiponitrile by the  
 catalytic hydrocyanation of 1,3-butadiene  
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Haderlein, Gerd;  
 Flores, Miguel Angel; Jungkamp, Tim; Luyken, Hermann;  
 Scheidel, Jens; Siegel, Wolfgang  
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany  
 SOURCE: PCT Int. Appl., 49 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073167	A1	20050811	WO 2005-EP717	20050126
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
DE 102004004682	A1	20050818	DE 2004-102004004682	20040129
CA 2553011	A1	20050811	CA 2005-2553011	20050126
EP 1713759	A1	20061025	EP 2005-701177	20050126
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS			
CN 1914160	A	20070214	CN 2005-80003694	20050126
BR 2005007184	A	20070626	BR 2005-7184	20050126
JP 2007519663	T	20070719	JP 2006-550078	20050126
MX 2006PA07756	A	20060926	MX 2006-PA7756	20060706
KR 2007011279	A	20070124	KR 2006-715317	20060728
IN 2006CN03131	A	20070727	IN 2006-CN3131	20060829
PRIORITY APPLN. INFO.:			DE 2004-102004004682A	20040129
			WO 2005-EP717	W 20050126

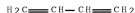
OTHER SOURCE(S): CASREACT 143:195577  
 AB A method for the production of adiponitrile by hydrocyanation of 1,3-butadiene over a catalyst is described where, in a first step, 1,3-butadiene is hydrocyanated into 3-pentenitrile over at least one elemental nickel catalyst and, in a second step, the 3-pentenitrile intermediate is hydrocyanated to form adiponitrile over an elemental nickel catalyst with the addition of at least one Lewis acid. At least one of the elemental nickel catalysts used in the resp. steps is converted in the other step. Process flow diagrams are presented.  
 IC ICM C07C253-10  
 ICS C07C253-30  
 CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
 Section cross-reference(s): 23, 48, 67  
 ST adiponitrile manuf butadiene catalytic hydrocyanation  
 IT Alkadienes  
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical

- process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)  
(1,3-butadiene; method for the production of adiponitrile by the  
catalytic hydrocyanation of 1,3-butadiene using)
- IT Nitriles, preparation  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
(Physical, engineering or chemical process); PREP (Preparation); PROC  
(Process)  
(dinitriles, adiponitrile; method for the production of adiponitrile by the  
catalytic hydrocyanation of 1,3-butadiene)
- IT Hydrocyanation catalysts  
(elemental nickel complexes; method for the production of adiponitrile by  
the catalytic hydrocyanation of 1,3-butadiene)
- IT Hydrocyanation  
(method for the production of adiponitrile by the catalytic  
hydrocyanation of 1,3-butadiene)
- IT Distillation  
Distillation columns  
Extraction  
Isomerization  
(method for the production of adiponitrile by the catalytic  
hydrocyanation of 1,3-butadiene using)
- IT Lewis acids  
RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical,  
engineering or chemical process); PROC (Process); USES (Uses)  
(method for the production of adiponitrile by the catalytic  
hydrocyanation of 1,3-butadiene using)
- IT 111-69-3P, Adiponitrile  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
(Physical, engineering or chemical process); PREP (Preparation); PROC  
(Process)  
(method for the production of adiponitrile by the catalytic  
hydrocyanation of 1,3-butadiene)
- IT 4635-87-4P, 3-Pentenitrile 13284-42-9P, 2-Pentenitrile  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
(Physical, engineering or chemical process); RCT (Reactant); PREP  
(Preparation); PROC (Process); RACT (Reactant or reagent)  
(method for the production of adiponitrile by the catalytic  
hydrocyanation of 1,3-butadiene)
- IT 106-99-0, 1,3-Butadiene, reactions  
RL: EPR (Engineering process); PEP (Physical, engineering or chemical  
process); RCT (Reactant); PROC (Process); RACT (Reactant or  
reagent)  
(method for the production of adiponitrile by the catalytic  
hydrocyanation of 1,3-butadiene)
- IT 7646-85-7, Zinc chloride, processes 7718-54-9, Nickel chloride,  
processes  
RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical,  
engineering or chemical process); PROC (Process); USES (Uses)  
(method for the production of adiponitrile by the catalytic  
hydrocyanation of 1,3-butadiene using)
- IT 4403-61-6P, 2-Methyl-2-butenitrile 16529-56-9P, 2-Methyl-3-  
butenenitrile 28906-50-5P, Methylglutaronitrile  
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
(Physical, engineering or chemical process); RCT (Reactant); PREP  
(Preparation); PROC (Process); RACT (Reactant or reagent)  
(method for the production of adiponitrile by the catalytic  
hydrocyanation of 1,3-butadiene using)
- IT 74-90-8, Hydrogen cyanide, reactions  
RL: EPR (Engineering process); PEP (Physical, engineering or chemical  
process); RCT (Reactant); PROC (Process); RACT (Reactant or

reagent)  
 (method for the production of adiponitrile by the catalytic  
 hydrocyanation of 1,3-butadiene using)  
 IT 4635-87-4P, 3-Pentenitrile  
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP  
 (Physical, engineering or chemical process); RCT (Reactant); PREP  
 (Preparation); PROC (Process); RACT (Reactant or reagent)  
 (method for the production of adiponitrile by the catalytic  
 hydrocyanation of 1,3-butadiene)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



IT 106-99-0, 1,3-Butadiene, reactions  
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical  
 process); RCT (Reactant); PROC (Process); RACT (Reactant or  
 reagent)  
 (method for the production of adiponitrile by the catalytic  
 hydrocyanation of 1,3-butadiene)  
 RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



IT 74-90-6, Hydrogen cyanide, reactions  
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical  
 process); RCT (Reactant); PROC (Process); RACT (Reactant or  
 reagent)  
 (method for the production of adiponitrile by the catalytic  
 hydrocyanation of 1,3-butadiene using)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



REFERENCE COUNT: 13 THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS  
 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 9 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 9  
 ACCESSION NUMBER: 2005:729613 CAPLUS Full-text  
 DOCUMENT NUMBER: 143:195576  
 TITLE: Catalytic hydrocyanation method for the production  
 of pentenenitriles from 1,3-butadiene and hydrogen  
 cyanide  
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Haderlein, Gerd;



PATENT ASSIGNEE(S): Schindler, Goetz-Peter; Jungkamp, Tim; Luyken, Hermann; Scheidel, Jens; Brodhagen, Andreas  
 SOURCE: BASF Aktiengesellschaft, Germany  
 PCT Int. Appl., 31 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073166	A2	20050811	WO 2005-EP773	20050127
WO 2005073166	A3	20070301		
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW, SM			
RM:	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
DE 102004004697	A1	20050818	DE 2004-102004004697	20040129
EP 1716102	A2	20061102	EP 2005-701202	20050127
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, PL, SK, BA, HR, IS, YU			
CN 1997624	A	20070711	CN 2005-80003692	20050127
JP 2007522122	T	20070809	JP 2006-550096	20050127
PRIORITY APPLN. INFO.:			DE 2004-102004004697A	20040129
			WO 2005-EP773	W 20050127

OTHER SOURCE(S): CASREACT 143:195576

AB A method is described for the hydrocyanation of 1,3-butadiene into pentenenitriles using at least one elemental Ni complex with phosphorous-containing ligands as a catalyst, where the 1,3-butadiene is used in a mixture with butane and the mixture contains 60-90 volume% 1,3-butadiene and 10-40 volume% butane.

IC ICM C07C253-00

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

ST Section cross-reference(s): 23, 67

ST pentenenitrile manuf catalytic hydrocyanation butadiene

IT Hydrocyanation  
 (catalytic hydrocyanation method for the production of pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT Hydrocyanation catalysts  
 (elemental Ni complexes and P-containing ligands; catalytic hydrocyanation method for the production of pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT Petroleum products  
 (gases, liquefied; in a catalytic hydrocyanation method for the production of pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT Phosphines  
 Phosphites  
 RL: CAT (Catalyst use); USES (Uses)  
 (ligands; in a catalytic hydrocyanation method for the production of pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT Nitriles, preparation

- RL: IMF (Industrial manufacture); PREP (Preparation)  
(unsatd., pentenenitriles; catalytic hydrocyanation method  
for the production of pentenenitriles from 1,3-butadiene and hydrogen  
cyanide)
- IT 1295-35-8 509083-87-8  
RL: CAT (Catalyst use); USES (Uses)  
(catalytic hydrocyanation method for the production of  
pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-  
butenenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(catalytic hydrocyanation method for the production of  
pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT 106-97-8, Butane, reactions  
RL: NUU (Other use, unclassified); RCT (Reactant); RACT (Reactant or  
reagent); USES (Uses)  
(catalytic hydrocyanation method for the production of  
pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(catalytic hydrocyanation method for the production of  
pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT 4635-87-4P, 3-Pentenenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(catalytic hydrocyanation method for the production of  
pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- RN 4635-87-4 CAPLUS  
CN 3-Pentenenitrile (CA INDEX NAME)



- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: RCT (Reactant); PACT (Reactant or reagent)  
(catalytic hydrocyanation method for the production of  
pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)



- RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 10 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 10

ACCESSION NUMBER: 2003:319912 CAPLUS Full-text

DOCUMENT NUMBER: 138:321395

TITLE: Phosphonites, use thereof as ligand in transition metal complexes and method for production of nitriles

INVENTOR(S): Bartsch, Michael; Baumann, Robert; Kunsmann-Keitel, Dagmar Pascale; Haderlein, Gerd; Jungkamp, Tim; Altmayer, Marco; Siegel, Wolfgang; Molnar, Ferenc

PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany

SOURCE: PCT Int. Appl., 32 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2003033509	A1	20030424	WO 2002-EP11107	20021004
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
DE 10150281	A1	20030430	DE 2001-10150281	20011012
DE 10207165	A1	20030821	DE 2002-10207165	20020220
CA 2464710	A1	20030424	CA 2002-2464710	20021004
AU 2002362815	A1	20030428	AU 2002-362815	20021004
EP 1438317	A1	20040721	EP 2002-801308	20021004
EP 1438317	B1	20060621		
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK			
BR 2002012965	A	20041013	BR 2002-12965	20021004
JP 2005505630	T	20050224	JP 2003-536248	20021004
CN 1639176	A	20050713	CN 2002-819907	20021004
AT 330962	T	20060715	AT 2002-801308	20021004
ES 2266630	T3	20070301	ES 2002-2801308	20021004
MX 2004PA02139	A	20040629	MX 2004-PA2139	20040305
US 2005090678	A1	20050428	US 2004-491918	20040408
US 7067685	B2	20060627		
IN 2004CN01004	A	20060203	IN 2004-CN1004	20040511
PRIORITY APPLN. INFO.:			DE 2001-10150281	A 20011012
			DE 2002-10207165	A 20020220
			WO 2002-EP11107	W 20021004

OTHER SOURCE(S): CASREACT 138:321395; MARPAT 138:321395

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\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

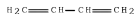
- AB The invention relates to phosphinites I and II (R1, R2, R5, R6, R7, R8, R9 = independently represent H, C1-8 alkyl or alkylene, or C1-8 alkoxy; R3 = H, Me; R4 = i-Pr, t-butyl; X = F, Cl or CF3; n = 1, 2) useful as cocatalysts for nickel catalyzed preparation of nitriles. Thus, nickel(0)/phosphonite-catalyzed isomerization of 2-methyl-3-butenenitrile to give 3-pentenitrile and same catalyst mediated hydrocyanation of 3-pentenitrile to give adipodinitrile is described.
- IC ICM C07F009-48  
ICS C07C253-10; B01J031-18
- CC 29-7 (Organometallic and Organometalloidal Compounds)  
Section cross-reference(s): 23, 67
- ST phosphonite nickel catalyzed isomerization hydrocyanation; nitrile dinitrile prep
- IT Hydrocyanation catalysts  
Isomerization catalysts  
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT Nitriles, preparation  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 7646-85-7, Zinc dichloride, uses  
RL: CAT (Catalyst use); USES (Uses)  
(additive; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 106-39-0, 1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 4635-87-4P, 3-Pentenitrile  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 16529-56-9, 2-Methyl-3-butenenitrile  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(isomerization; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 592-51-8P, 4-Pentenitrile 16529-66-1P, trans-3-Pentenitrile 16545-73-1P, cis-3-Pentenitrile 20068-02-4P, cis-2-Methyl-2-butenenitrile 26294-98-4P, trans-2-Pentenitrile 28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile  
RL: BYP (Byproduct); PREP (Preparation)  
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 1295-35-8, Bis(1,5-cyclooctadiene)nickel 125280-25-3 494227-34-8 512172-91-7 512172-92-8 512172-93-9 512172-94-0 512172-95-1  
RL: CAT (Catalyst use); USES (Uses)  
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 74-90-6, Hydrogen cyanide, reactions  
RL: PCT (Reactant); RACT (Reactant or reagent)  
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 111-69-3P, Adipodinitrile  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 106-99-0, 1,3-Butadiene, reactions

10/586490

RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation; use of phosphonites as cocatalysts in nickel  
complex catalyzed production of nitriles)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4E, 3-Pentenitrile

RL: RCT (Reactant); SPN (Synthetic preparation); PREP  
(Preparation); RACT (Reactant or reagent)  
(hydrocyanation; use of phosphonites as cocatalysts in nickel  
complex catalyzed production of nitriles)

RN 4635-87-4 CAPLUS

CN 3-Pentenitrile (CA INDEX NAME)



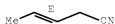
IT 16529-66-1P, trans-3-Pentenitrile 16545-78-1P,  
cis-3-Pentenitrile

RL: BYP (Byproduct); PREP (Preparation)  
(use of phosphonites as cocatalysts in nickel complex  
catalyzed production of nitriles)

RN 16529-66-1 CAPLUS

CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 CAPLUS

CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
(use of phosphonites as cocatalysts in nickel complex  
catalyzed production of nitriles)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)

N  
CH

REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 11 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 11  
 ACCESSION NUMBER: 1995:854364 CAPLUS Full-text  
 DOCUMENT NUMBER: 124:55389  
 TITLE: Vapor phase hydrocyanation of diolefinic compounds catalyzed by nickel complexes with bidentate phosphite ligands  
 INVENTOR(S): Druliner, Joe D.  
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA  
 SOURCE: U.S., 7 pp.  
 CODEN: USXXAM  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5449807	A	19950912	US 1994-342195	19941118
CA 2200700	A1	19960530	CA 1995-2200700	19951101
CA 2200700	C	20070109		
WO 9616022	A1	19960530	WO 1995-US14787	19951101
W: BR, CA, CN, JP, KR, SG				
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
EP 792259	A1	19970903	EP 1995-941390	19951101
EP 792259	B1	19990804		
R: AT, BE, CH, DE, ES, FR, GB, IT, LI, NL, SE				
CN 1163606	A	19971029	CN 1995-196276	19951101
CN 1068307	B	20010711		
BR 9510347	A	19971223	BR 1995-10347	19951101
JP 10509954	T	19980929	JP 1995-516952	19951101
AT 182881	T	19990815	AT 1995-941390	19951101
ES 2138761	T3	20000116	ES 1995-941390	19951101
JP 3478399	B2	20031215	JP 1996-516952	19951101
PRIORITY APPLN. INFO.:			US 1994-342195	A 19941118
			WO 1995-US14787	W 19951101
OTHER SOURCE(S):		CASREACT 124:55389; MARPAT 124:55389		
GI				

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB A process is claimed for the gas-phase hydrocyanation of diolefinic compds. comprising, reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase within a temperature range of 135-170° in the presence of a supported catalyst composition comprising zero-valent nickel and at least one bidentate phosphite ligand selected from the group represented by I wherein each R1, independently, is a secondary or tertiary hydrocarbyl of 3

to 12 carbon atoms; each R2, independently, is H, a C1 to C12 alkyl, or OR3, wherein R3 is C1 to C12 alkyl; and II wherein each R4, independently, is a tertiary hydrocarbon of up to 12 carbon atoms, or OR5, wherein R5 is a C1 to C12 alkyl; and each R6, independently, is a tertiary hydrocarbon of up to 12 carbon atoms, to produce acyclic olefinic nitriles in which the olefinic double bond is not conjugated with the cyano group. Thus, e.g., hydrocyanation of 1,3-butadiene catalyzed by silica-supported Ni(0)LCH2:CH2 with L = II (R4 = OMe, R6 = tert-Bu) (preparation given) resulted, after 1,5 h, in 76.4% conversion of BD and 90.4% conversion to pentenenitriles [3- + 4-pentenitrile + 2-methyl-3-butenitrile]; no pentenenitrile products were observed when a zinc copper chromite catalyst was used.

IC ICM C07C253-10  
INCL 558338000  
CC 23-19 (Aliphatic Compounds)  
Section cross-reference(s): 35  
ST pentenenitrile; butadiene hydrocyanation nickel bidentate phosphite catalyst  
IT Hydrocyanation catalysts  
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)  
IT 1344-28-1, Alumina, uses 7440-44-0, Carbon, uses 7631-86-9, Silica, uses  
RL: CAT (Catalyst use); USES (Uses)  
(catalyst support; vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)  
IT 169254-14-2P  
RL: BYP (Byproduct); PREP (Preparation)  
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)  
IT 169254-15-3P  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)  
IT 592-51-8P, 4-Pentenitrile 4635-87-4P, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile  
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)  
IT 74-85-1, Ethene, reactions 74-90-8, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions 121627-17-6  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)  
IT 1344-28-1, Alumina, uses  
RL: CAT (Catalyst use); USES (Uses)  
(catalyst support; vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)  
RN 1344-28-1 CAPLUS  
CN Aluminum oxide (Al2O3) (CA INDEX NAME)

\*\*\* STRUCTURE DIAGRAM IS NOT AVAILABLE \*\*\*

IT 4635-87-4P, 3-Pentenitrile  
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)  
RN 4635-87-4 CAPLUS  
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-3, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: FCT (Reactant); FACT (Reactant or reagent);  
(vapor phase hydrocyanation of butadiene catalyzed by nickel  
complexes with bidentate phosphite ligands)  
RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 12 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 12  
ACCESSION NUMBER: 1988:131003 CAPLUS Full-text  
DOCUMENT NUMBER: 108:131003  
TITLE: The stereochemistry of organometallic compounds.  
XXVIII. The nickel-catalyzed addition of hydrogen  
cyanide to aliphatic dienes  
AUTHOR(S): Campi, Eva M.; Elmes, Patricia S.; Jackson, W. Roy;  
Lovel, Craig G.; Probert, Michael K. S.  
CORPORATE SOURCE: Dep. Chem., Monash Univ., Clayton, 3168, Australia  
SOURCE: Australian Journal of Chemistry (1987), 40(6), 1053-61  
CODEN: AJCHAS; ISSN: 0004-9425  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 108:131003  
AB Hydrocyanation of a variety of aliphatic dienes, e.g. (H2C:CH)2CH2, in the  
presence of Ni(0) complexes gave diene rearrangement products and  $\beta,\gamma$ -unsatd.  
nitriles, e.g. MeCH:CHCHMeCN, in 10-90% yields. The use of chiral Ni complexes  
gave only low levels of asym. induction. A mechanism involving  $\pi$ -allyl Ni  
intermediates is proposed.  
CC 23-19 (Aliphatic Compounds)  
ST diene hydrocyanation nickel catalyst; nitrile unsatd; regiochem diene  
hydrocyanation mechanism  
IT Hydrocyanation catalysts  
(nickel complexes, for dienes to unsatd. nitriles)  
IT 84786-32-3 113065-29-5  
RL: CAT (Catalyst use); USES (Uses)  
(catalyst, for hydrocyanation of dienes)



IT 14221-00-2  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts, for hydrocyanation of butadiene and pentadiene)

IT 101-02-0, Triphenylphosphite 32305-98-9 62144-65-4  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (co-catalyst, for hydrocyanation of dienes)

IT 74-90-8, Hydrogen cyanide, reactions 75-86-5, Acetone  
 cyanohydrin 3017-23-0, Deuterium cyanide  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation by, of dienes, in the presence of nickel complexes)

IT 106-99-0, Buta-1,3-diene, reactions 591-93-5, Penta-1,4-diene  
 592-42-7, Hexa-1,5-diene 1647-16-1 3710-30-3, Octa-1,7-diene  
 5194-51-4 7319-00-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation of, in the presence of nickel complexes)

IT 74-90-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation, of dienes, unsatd. nitriles by)

IT 816-16-0P, Methyl 2-ethylpentanoate 816-63-7P 2177-81-3P, Methyl  
 2-methylhexanoate 2177-86-8P, Methyl 2-methyloctanoate 5162-60-7P  
 7732-18-5P, Water, preparation 16529-56-9P, 2-Methylbut-3-enenitrile  
 16529-66-1P 74669-69-5P 80651-37-2P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)

IT 74-90-8, Hydrogen cyanide, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation by, of dienes, in the presence of nickel complexes)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, Buta-1,3-diene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation of, in the presence of nickel complexes)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 74-90-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation, of dienes, unsatd. nitriles by)

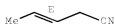
RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 16529-66-1P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)  
 RN 16529-66-1 CAPLUS  
 CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



L88 ANSWER 13 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2005:729626 CAPLUS Full-text  
 DOCUMENT NUMBER: 143:195589  
 TITLE: Vacuum distillation method for the separation of  
 pentenenitrile isomers  
 INVENTOR(S): Jungkamp, Tim; Baumann, Robert; Bartsch, Michael;  
 Haderlein, Gerd; Luyken, Hermann; Scheidel, Jens  
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany  
 SOURCE: PCT Int. Appl., 33 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073179	A1	20050811	WO 2005-EP726	20050126
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RM:	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
DE 102004004721	A1	20050818	DE 2004-102004004721	20040129
CA 2553776	A1	20050811	CA 2005-2553776	20050126
EP 1713766	A1	20061025	EP 2005-707007	20050126
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS			
CN 1914167	A	20070214	CN 2005-80003676	20050126
BR 2005007196	A	20070626	BR 2005-7196	20050126
JP 2007519667	T	20070719	JP 2006-550083	20050126
MX 2006PA07754	A	20060926	MX 2006-PA7754	20060706
US 2007112215	A1	20070517	US 2006-586452	20060718
IN 2006CN03127	A	20070608	IN 2006-CN3127	20060829
PRIORITY APPLN. INFO.:			DE 2004-102004004721A	20040129
			WO 2005-EP726	W 20050126

- AB A vacuum distillation method for the separation of material mixts. of pentenenitrile isomers, prepared by the catalytic hydrocyanation of 1,3-butadiene with HCN, is described where at least one isomer of the mixture (e.g., 3-pentenenitrile) is enriched and the separation of the mixture of pentenenitrile mixts. is carried out by distillation at reduced pressures.
- IC ICM C07C253-34  
ICS C07C255-07
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 48
- IT Hydrocyanation catalysts  
(hydrocyanation of 1,3-butadiene into pentenenitrile isomers using)
- IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P, cis-2-Methyl-2-butenenitrile 25899-50-7P, cis-2-Pentenenitrile 27236-41-5P, Pentenenitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile  
RL: PEP (Physical, engineering or chemical process); PNU (Preparation, unclassified); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
(vacuum distillation method for the separation of pentenenitrile isomers)
- IT 74-90-8, Hydrogen cyanide, reactions 166-99-0, 1,3-Butadiene, reactions  
RL: PCT (Reactant); RACT (Reactant or reagent)  
(vacuum distillation method for the separation of pentenenitrile isomers prepared from)
- IT 4635-87-4P, 3-Pentenenitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile  
RL: PEP (Physical, engineering or chemical process); PNU (Preparation, unclassified); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
(vacuum distillation method for the separation of pentenenitrile isomers)
- RN 4635-87-4 CAPLUS
- CN 3-Pentenenitrile (CA INDEX NAME)



- RN 16529-66-1 CAPLUS
- CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



- RN 16545-78-1 CAPLUS
- CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.

10/586490



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(vacuum distillation method for the separation of pentenenitrile isomers  
prepared from)  
RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 14 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:729625 CAPLUS Full-text

DOCUMENT NUMBER: 143:195588

TITLE: Recovery of hydrogen cyanide from 1,3-butadiene  
catalytic hydrocyanation reaction mixtures in the  
manufacture of 3-pentenenitriles by azeotropic  
distillation

INVENTOR(S): Jungkamp, Tim; Polka, Hans-Martin; Baumann, Robert;  
Bartsch, Michael; Haderlein, Gerd; Luyken, Hermann;  
Scheidel, Jens

PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany

SOURCE: PCT Int. Appl., 24 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005073178	A2	20050811	WO 2005-EP724	20050126
WO 2005073178	A3	20050922		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,				

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SI, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW  
 RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

DE 102004004718	A1	20050818	DE 2004-102004004718	20040129
CA 2553766	A1	20050811	CA 2005-2553766	20050126
EP 1716109	A2	20061102	EP 2005-715209	20050126
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS				
CN 1914166	A	20070214	CN 2005-80003623	20050126
BR 2005007194	A	20070626	BR 2005-7194	20050126
JP 2007519665	T	20070719	JP 2006-550081	20050126
MX 2006PA07887	A	20061002	MX 2006-PA7887	20060710
IN 2006CN03124	A	20070608	IN 2006-CN3124	20060829

PRIORITY APPLN. INFO.: DE 2004-102004004718A 20040129  
 WO 2005-EP724 W 20050126

OTHER SOURCE(S): CASREACT 143:195588

AB A method is described for separating hydrogen cyanide from mixts. containing 3-pentenitrile by means of the azeotropic distillation of hydrogen cyanide with 1,3-butadiene.

IC ICM C07C253-34

ICS C07C255-04; C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 48

IT Hydrocyanation catalysts

(Ni-P complexes; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)

IT Distillation

(azeotropic; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)

IT Hydrocyanation

(recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)

IT Nitriles, preparation

RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process) (unsatd., 3-pentenitriles; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)

IT 106-99-0F, 1,3-Butadiene, preparation

RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); RCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or reagent); USES (Uses)

(azeotropic distillation agent; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)

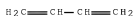
IT 509083-87-8

RL: CAT (Catalyst use); USES (Uses)

(ligand; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)

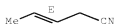
IT 7440-02-0, Nickel, uses

- RL: CAT (Catalyst use); USES (Uses)  
(recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)
- IT 16529-66-1P, trans-3-Pentenitrile 27236-41-5P, Pentenenitrile  
RL: IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
(recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)
- IT 16529-56-9P, 2-Methyl-3-butenitrile  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); RCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or reagent); USES (Uses)  
(recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)
- IT 74-90-6P, Hydrogen cyanide, preparation  
RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); RCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)  
(recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)
- IT 106-99-0P, 1,3-Butadiene, preparation  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); RCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or reagent); USES (Uses)  
(azeotropic distillation agent; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)
- RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



- IT 16529-66-1P, trans-3-Pentenitrile  
RL: IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)  
(recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)
- RN 16529-66-1 CAPLUS  
CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-3P, Hydrogen cyanide, preparation  
 RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or reagent) (recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenitriles by azeotropic distillation)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 15 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:409533 CAPLUS Full-text

DOCUMENT NUMBER: 142:430424

TITLE: Design and preparation of sterically hindered chelate phosphinite-phosphite ligands for nickel-catalyzed preparation of nitriles and dinitriles by hydrocyanation of unsaturated compounds

INVENTOR(S): Bartsch, Michael; Baumann, Robert; Haderlein, Gerd; Flores, Miguel Angel; Jungkamp, Tim; Luyken, Hermann; Scheidel, Jens; Siegel, Wolfgang

PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany

SOURCE: PCT Int. Appl., 33 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

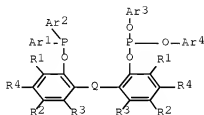
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005042547	A1	20050512	WO 2004-EP12176	20041028
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
DE 10350999	A1	20050602	DE 2003-10350999	20031030
CA 2543673	A1	20050512	CA 2004-2543673	20041028
EP 1682559	A1	20060726	EP 2004-790949	20041028
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK				
CN 1875025	A	20061206	CN 2004-80032095	20041028
BR 2004016080	A	20070102	BR 2004-16080	20041028
JP 2007509886	T	20070419	JP 2006-537184	20041028
MX 2006PA03939	A	20060703	MX 2006-PA3939	20060407

US 2007060766	A1	20070315	US 2006-577138	20060425
IN 2006CN01887	A	20070223	IN 2006-CN1887	20060529
PRIORITY APPLN. INFO.:			DE 2003-10350999	A 20031030
			WO 2004-EP12176	W 20041028

OTHER SOURCE(S): MARPAT 142:430424

GI



I

AB The 2,2'-biphenol, 2,2'-methylenebis(phenol) and 2,2'-binaphthol-bridged phosphinite-phosphite ligands, preferably of the type I (Ar1, Ar2 = Ph, fluoro- and trifluoromethyl-substituted Ph, preferably 3-FC6H4, 3,5-F2C6H3, 3-(CF3)C6H4, 3,5-(CF3)2C6H3; Ar3 = Ar4 = 2-MeC6H4; Q = (CH2)n, where n = 0, 1; R1, R2, R4 = H, C1-8 (un)saturated hydrocarbyl; R3 = H, Me, Et; or R2-R3 = (CH)4, same R1, R2, R4) are designed for nickel(0)-catalyzed hydrocyanation of butadiene to give 3-pentenitrile and adiponitrile in the presence of Lewis acid promoters, such as metal chlorides and triflates. In an example, ligand of the type I (2, Ar1 = Ar2 = Ph, Ar3 = Ar4 = 2-MeC6H4, R1 = R2 = Me, R3 = R4 = H) was prepared by reaction of 3,3',5,5'-tetramethyl-2,2'-biphenol with Ph2PCl and (2-MeC6H4O)2PCl in toluene at -15°. Hydrocyanation of 1,3-butadiene by HCN catalyzed by Ni(cod)2/2 (1:3 mol. ratio; C4H6/HCN = 1.6:1; 0.135 mol % of the catalyst) gave a 1.5:1 mixture of 2-methyl-3-butenitrile and 3-pentenitrile; the ratio was enhanced to 1:4.6 upon isomerization during 1 h at 115°. In another example, 3-pentenitrile was hydrocyanated to adiponitrile with the same catalyst at 25° for 88 min in the presence of ZnCl2 with regioselectivity of 91.3%. In comparison examples, use of o- and m-tolyl phosphine nickel(0) complex gave only 79.6% selectivity on adiponitrile.

ICM C07F009-50

ICS C07F009-12; B01J031-24

CC 29-7 (Organometallic and Organometalloidal Compounds)

Section cross-reference(s): 23

ST phosphorus ligand bidentate diene unsatd nitrile hydrocyanation catalyst; nitrile dinitrile improved prepn process phosphinite phosphite ligand catalyst; nickel catalyzed hydrocyanation phosphinite phosphite bidentate sterically hindered ligand; butadiene pentenenitrile hydrocyanation improved process nickel phosphinite phosphite catalyst; isomerization unsatd nitrile hydrocyanation nickel phosphinite phosphite catalyst; adiponitrile improved prepn regioselective hydrocyanation process nickel catalyst; addn reaction diene unsatd nitrile hydrocyanation adiponitrile improved prepn

IT Ligands

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);

USES (Uses)

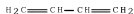
(bidentate, phosphinites, phosphites; design and preparation of sterically hindered phosphinite-phosphite bidentate chelate ligands for nickel-



- catalyzed hydrocyanation of dienes and unsatd. nitriles  
improved process)
- IT Addition reaction  
Hydrocyanation  
Hydrocyanation catalysts  
Regiochemistry  
(design and preparation of sterically hindered phosphinite-phosphite  
bidentate chelate ligands for nickel-catalyzed hydrocyanation  
of dienes and unsatd. nitriles improved process)
- IT Chelates  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)  
(design and preparation of sterically hindered phosphinite-phosphite  
bidentate chelate ligands for nickel-catalyzed hydrocyanation  
of dienes and unsatd. nitriles improved process)
- IT Alkadienes  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(design and preparation of sterically hindered phosphinite-phosphite  
bidentate chelate ligands for nickel-catalyzed hydrocyanation  
of dienes and unsatd. nitriles improved process)
- IT Steric hindrance  
(design and preparation of sterically hindered phosphinite-phosphite  
bidentate ligands for nickel-catalyzed hydrocyanation of  
dienes and unsatd. nitriles improved process)
- IT Nitriles, preparation  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(dinitriles; design and preparation of sterically hindered  
phosphinite-phosphite bidentate chelate ligands for nickel-  
catalyzed hydrocyanation of dienes and unsatd. nitriles  
improved process)
- IT Isomerization  
(double bond migration in unsatd. nitriles catalyzed by  
sterically hindered phosphinite-phosphite bidentate nickel complexes in  
improved process for regioselective hydrocyanation of butadiene)
- IT Phosphorus acids  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)  
(esters, phosphinites; design and preparation of sterically hindered  
phosphinite-phosphite bidentate chelate ligands for nickel-  
catalyzed hydrocyanation of dienes and unsatd. nitriles  
improved process)
- IT Phosphites  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)  
(phosphinites, phosphites; design and preparation of sterically hindered  
phosphinite-phosphite bidentate chelate ligands for nickel-  
catalyzed hydrocyanation of dienes and unsatd. nitriles  
improved process)
- IT Nitriles, preparation  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
(Reactant or reagent)  
(unsatd.; isomerization and hydrocyanation of unsatd. nitriles  
catalyzed by nickel phosphinite-phosphite bidentate chelate  
complexes in adiponitrile improved preparation process)
- IT 26567-10-2 110932-47-3  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(esterification; regioselective hydrocyanation of butadiene and unsatd.  
nitriles catalyzed by phosphinite-phosphite bidentate chelate  
nickel complexes in improved process for preparation of adiponitrile)
- IT 74-90-3, Hydrocyanic acid, reactions 186-99-0,

- 1,3-Butadiene, reactions  
 RL: RCT (Reactant); PACT (Reactant or reagent)  
 (hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- IT 592-51-8P, 4-Pentenitrile  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- IT 4635-87-4P, 3-Pentenitrile  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (isomerization, hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- IT 16529-56-9P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (isomerization; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- IT 7440-02-0D, Nickel, complexes, phosphinite-phosphite 7646-85-7, Zinc chloride, uses  
 RL: CAT (Catalyst use); USES (Uses)  
 (regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- IT 851024-54-9P 851024-55-0P 851024-56-1P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- IT 111-69-3P, Adiponitrile  
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
 (regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- IT 1079-66-9, Chlorodiphenylphosphine 1295-35-8 22277-50-5 33104-14-2  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- IT 74-90-8, Hydrocyanic acid, reactions 106-99-0, 1,3-Butadiene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)

RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4E, 3-Pentenitrile  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP  
 {Preparation}; RACT (Reactant or reagent)  
 (isomerization, hydrocyanation; regioselective hydrocyanation of  
 butadiene and unsatd. nitriles catalyzed by  
 phosphinite-phosphite bidentate chelate nickel complexes in improved  
 process for preparation of adiponitrile)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS  
 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 16 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:737717 CAPLUS Full-text  
 DOCUMENT NUMBER: 139:262467  
 TITLE: Phosphonite ligands and their use in hydrocyanation  
 INVENTOR(S): Lenges, Christian P.; Lu, Helen S. M.; Ritter, Joachim  
 C.  
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA  
 SOURCE: PCT Int. Appl., 25 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2003076394	A1	20030918	WO 2003-US7033	20030307
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
US 2003195371	A1	20031016	US 2002-93655	20020307
US 6660877	B2	20031209		

10/586490

TW 266650	B	20061121	TW 2002-91138062	20021231
AU 2003218000	A1	20030922	AU 2003-218000	20030307
US 2003195372	A1	20031016	US 2003-454074	20030604
US 6737539	B2	20040518		
US 2003212288	A1	20031113	US 2003-454024	20030604
US 6846945	B2	20050125		

PRIORITY APPLN. INFO.:

US 2002-93655	A	20020307
WO 2003-US7033	W	20030307

OTHER SOURCE(S): MARPAT 139:262467

AB Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter. Thus, trans-3-pentenitrile was reacted in the presence of bis(1,5- cyclooctadiene) nickel, phosphonite bidentate ligand, and zinc dichloride to give an adiponitrile.

IC ICM C07C253-00

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

ST organometallic multidentate phosphonite ligand hydrocyanation catalyst isomerization olefin

IT Hydrocyanation catalysts

Isomerization catalysts

(phosphonite ligands and their use in hydrocyanation)

IT Hydrocyanation catalysts

(stereoselective; phosphonite ligands and their use in hydrocyanation)

IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenitrile 4635-87-4P

, 3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile

RL: IMF (Industrial manufacture); PREP (Preparation)

(phosphonite ligands and their use in hydrocyanation)

IT 16529-56-9P, 2-Methyl-3-butenitrile 16529-66-1P,

trans-3-Pentenitrile

RL: IMF (Industrial manufacture); RCT (Reactant); PREP

(Preparation); RACT (Reactant or reagent)

(phosphonite ligands and their use in hydrocyanation)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,

1,3-Butadiene, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(phosphonite ligands and their use in hydrocyanation)

IT 4635-87-4P, 3-Pentenitrile 16545-78-1P,

cis-3-Pentenitrile

RL: IMF (Industrial manufacture); PREP (Preparation)

(phosphonite ligands and their use in hydrocyanation)

RN 4635-87-4 CAPLUS

CN 3-Pentenitrile (CA INDEX NAME)



RN 16545-78-1 CAPLUS

CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

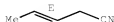
Double bond geometry as shown.



10/586490

IT 16529-66-1P, trans-3-Pentenitrile  
RL: IMF (Industrial manufacture); RCT (Reactant); PPEP  
{Preparation}; RACT (Reactant or reagent)  
(phosphonite ligands and their use in hydrocyanation)  
RN 16529-66-1 CAPLUS  
CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(phosphonite ligands and their use in hydrocyanation)  
RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 17 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2003:223752 CAPLUS [Full-text](#)

DOCUMENT NUMBER: 138:254847

TITLE: Process for manufacture of nitrile and dinitrile  
compounds by reaction of alkenes or unsaturated  
nitriles with hydrogen cyanide in ionic liquid  
solvents and application to the production of  
adiponitrile

INVENTOR(S): Basset, Jean Marie; Chauvin, Yves; Galland, Jean  
Christophe

PATENT ASSIGNEE(S): Rhodia Polyamide Intermediates, Fr.

SOURCE: Fr. Demande, 22 pp.

CODEN: FRXXBL

DOCUMENT TYPE: Patent

LANGUAGE: French

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
FR 2829763	A1	20030321	FR 2001-12040	20010918
FR 2829763	B1	20041203		
WO 2003024919	A1	20030327	WO 2002-FR3166	20020917
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2002342980	A1	20030401	AU 2002-342980	20020917
EP 1427695	A1	20040616	EP 2002-779637	20020917
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK				
CN 1564807	A	20050112	CN 2002-819851	20020917
JP 2005503410	T	20050203	JP 2003-528767	20020917
RU 2265591	C2	20051210	RU 2004-111655	20020917
IN 2004CN00554	A	20051223	IN 2004-CN554	20040315
US 2004260112	A1	20041223	US 2004-489838	20040818
PRIORITY APPLN. INFO.:			FR 2001-12040	A 20010918
			WO 2002-FR3166	W 20020917

OTHER SOURCE(S): CASREACT 138:254847

AB The invention relates to the manufacture of nitriles from unsatd. organic compds. by reaction with HCN. In particular, it relates to manufacture of nitriles used in the synthesis of adiponitrile, an important chemical intermediate for the manufacture of, e.g., hexamethylenediamine and  $\epsilon$ -caprolactam. The process provides compds. containing  $\geq 1$  nitrile function by hydrocyanation, with HCN, of an organic compound containing  $\geq 1$  ethylenic unsatn. The reaction takes place in the presence of a catalytic system comprising nickel, platinum, or palladium, and an organophosphorus ligand, using an ionic liquid reaction medium. A Lewis acid cocatalyst, functioning as an isomerization catalyst for unsatd. nitriles, may also be present. This cocatalyst provides for isomerization of undesired branched unsatd. nitriles to give preferred linear isomers, which undergo hydrocyanation to give adiponitrile. The anion of the ionic solvent may also function as a Lewis acid. For instance, the ionic liquid 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide (I) was prepared in 90% yield from the corresponding imidazolium chloride and lithium amide salts in water at room temperature. I and 2 other imidazolium salts were prepared and tested as solvents and isomerization catalysts in a representative hydrocyanation reaction mixture. Thus, a mixture of unsatd. C5 nitriles containing 79% 2-methyl-3-butenenitrile (II) was subjected to isomerization in a solution of I and heptane in the presence of Ni(COD)<sub>2</sub> (hydrocyanation catalyst) and 3-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na (ligand) at 100° for 3 h. The isomerization reaction gave 96% conversion of II, with a 94% yield of the desired linear isomers 3-pentenitrile (III) and 4-pentenitrile, with only 2.4% yield of undesired isomers. In a hydrocyanation reaction of III using the same catalyst and ligand, I as solvent, Me<sub>2</sub>C(OH)CN as the source of HCN, and added ZnCl<sub>2</sub> as an addnl. Lewis acid, desired dinitrile products (including adiponitrile) were obtained in 16.0% yield with 25.9% conversion of III.

IC ICM C07C255-04

CC 23-19 (Aliphatic Compounds)

Section cross-reference(s): 45

- ST nitrile unsatd hydrocyanation hydrogen cyanide liq ionic solvent;  
imidazolium ionic liq solvent hydrocyanation pentenenitrile; adiponitrile  
manuf ionic liq solvent imidazolium; isomerization methylbutenenitrile  
pentenenitrile Lewis acid catalyst; nickel palladium platinum phosphine  
ligand hydrocyanation catalyst ionic solvent
- IT Isomerization catalysts  
(Lewis acids; process for manufacture of nitriles by hydrocyanation of  
unsatd. compds. with HCN in ionic liquid solvents)
- IT Ligands  
RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES  
(Uses)  
(hydrocyanation catalyst component; process for manufacture of  
nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid  
solvents)
- IT Lewis acids  
RL: CAT (Catalyst use); USES (Uses)  
(isomerization cocatalyst; process for manufacture of nitriles by  
hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)
- IT Hydrocyanation catalysts  
(nickel, platinum, or palladium with organophosphorus ligands; process  
for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN  
in  
ionic liquid solvents)
- IT Organic compounds, reactions  
RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES  
(Uses)  
(phosphorus-containing, hydrocyanation catalyst ligands; process  
for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN  
in  
ionic liquid solvents)
- IT 122-52-1, Triethyl phosphite 603-35-0, Triphenylphosphine, reactions  
607-01-2, Diphenylethylphosphine 672-66-2, Dimethylphenylphosphine  
855-38-9, Tris(p-methoxyphenyl)phosphine 998-40-3, Tributylphosphine  
2622-14-2, Tricyclohexylphosphine 4712-55-4, Diphenyl phosphite  
7688-25-7, 1,4-Bis(diphenylphosphino)butane 26834-21-9,  
Tritolylphosphine 34684-16-7, Dimethyl-n-octylphosphine 63995-75-5,  
Sodium triphenylphosphinomono-m-sulfonate 226420-48-0,  
(3-Sodiosulfonatophenyl)diphenylphosphine 250788-83-1,  
(5-Sodiocarboxy-2-furyl)diphenylphosphine  
RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES  
(Uses)  
(hydrocyanation catalyst ligand; process for manufacture of  
nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid  
solvents)
- IT 1295-35-8, Di(1,5-cyclooctadiene)nickel 7440-02-0, Nickel, uses  
7440-05-3, Palladium, uses 7440-06-4, Platinum, uses  
RL: CAT (Catalyst use); USES (Uses)  
(hydrocyanation catalyst; process for manufacture of nitriles by  
hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)
- IT 106-99-0, 1,3-Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation substrate; process for manufacture of nitriles by  
hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)
- IT 960-71-4, Triphenylborane 1078-58-6, Diphenylzinc 7646-79-9, Cobalt  
dichloride, uses 7646-85-7, Zinc chloride, uses 54010-75-2, Zinc  
triflate 128008-30-0, Indium triflate  
RL: CAT (Catalyst use); USES (Uses)  
(isomerization cocatalyst; process for manufacture of nitriles by  
hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)
- IT 592-51-8P, 4-Pentenenitrile 4635-87-4P, 3-Pentenenitrile

RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (isomerization product and hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 74-90-8, Hydrogen cyanide, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 106-99-0, 1,3-Butadiene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenitrile  
 RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (isomerization product and hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 18 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2003:93132 CAPLUS Full-text  
 DOCUMENT NUMBER: 138:137726



10/586490

TITLE: Isomerization and hydrocyanation of monoolefinic C5-mononitriles in the presence of Ni(0)-phosphite/phosphonite catalysts

INVENTOR(S): Bartsch, Michael; Baumann, Robert; Kunsmann-Keitel, Dagmar Pascale; Haderlein, Gerd; Jungkamp, Tim; Altmayer, Marco; Siegel, Wolfgang

PATENT ASSIGNEE(S): BASF AG, Germany

SOURCE: Ger. Offen., 18 pp.  
CODEN: GWXXBX

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 10136488	A1	20030206	DE 2001-10136488	20010727
TW 570839	B	20040111	TW 2002-91115419	20020711
CA 2454912	A1	20030213	CA 2002-2454912	20020716
WO 2003011457	A1	20030213	WO 2002-EP7888	20020716
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2002355640	A1	20030217	AU 2002-355640	20020716
EP 1414567	A1	20040506	EP 2002-791454	20020716
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK				
BR 2002011455	A	20040817	BR 2002-11455	20020716
CN 1535179	A	20041006	CN 2002-814769	20020716
JP 2004535929	T	20041202	JP 2003-516681	20020716
MX 2004PA00559	A	20040420	MX 2004-PA559	20040119
US 2004176622	A1	20040909	US 2004-484169	20040120
IN 2004CN00391	A	20051223	IN 2004-CN391	20040226
PRIORITY APPLN. INFO.:			DE 2001-10136488	A 20010727
			WO 2002-EP7888	W 20020716

OTHER SOURCE(S): MARPAT 138:137726

AB Monoolefinic C5-mononitriles, e.g., 2-methyl-3-butenenitrile (readily available from hydrocyanation of 1,3-butadiene), was isomerized into a mixture of linear mononitrile, e.g., 3-pentenitrile (main) with improved selectivity in the presence of Ni(0) complexes with chelating bisphosphite or bisphosphonite ligands. The pentenenitrile isomers can be further hydrocyanated with HCN to the corresponding dinitriles, e.g., adiponitrile, with the same catalysts and ZnCl<sub>2</sub> promoter.

IC ICM B01J031-22

ICS B01J031-24; C07C253-10; C07B043-08

CC 35-2 (Chemistry of Synthetic High Polymers)  
Section cross-reference(s): 67

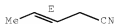
ST monoolefinic nitrile isomerization hydrocyanation dinitrile manuf; nickel phosphite catalyst nitrile isomerization hydrocyanation; phosphonite nickel catalyst nitrile isomerization hydrocyanation

IT Hydrocyanation catalysts  
Isomerization catalysts  
(catalysts for isomerization and hydrocyanation of nitriles)

10/586490

- IT Hydrocyanation  
Isomerization  
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT Nitriles, preparation  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 1295-35-8, Bis(1,5-cyclooctadienyl)nickel  
RL: CAT (Catalyst use); USES (Uses)  
(catalyst precursor; catalysts for isomerization and hydrocyanation of nitriles)
- IT 7646-85-7, Zinc chloride, uses  
RL: CAT (Catalyst use); USES (Uses)  
(catalyst promoter; catalysts for isomerization and hydrocyanation of nitriles)
- IT 620-38-2D, Tris(m-Tolyl)phosphite, complex with nickel 620-42-8D, p-Tolylphosphite, complex with nickel 7440-02-0D, Nickel, complexes with phosphite ligands 179259-60-0D, complex with nickel 220472-84-4D, complex with nickel 494227-34-8D, complex with nickel  
RL: CAT (Catalyst use); USES (Uses)  
(catalysts for isomerization and hydrocyanation of nitriles)
- IT 111-69-3P, Adipodinitrile 16529-66-1P, trans-3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile 20068-02-4P, cis-2-Methyl-2-butenitrile 25899-50-7P, cis-2-Pentenitrile 26294-98-4P, trans-2-Pentenitrile 28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 4635-87-4P, 3-Pentenitrile  
RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)  
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 74-90-8, Hydrocyanic acid, reactions 196-99-0, 1,3-Butadiene, reactions 16529-56-9, 2-Methyl-3-butenitrile  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 16529-66-1P, trans-3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- RN 16529-66-1 CAPLUS  
CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.

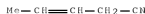


- RN 16545-78-1 CAPLUS  
CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



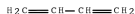
IT 4635-87-4R, 3-Pentenitrile  
 RL: IMF (Industrial manufacture); RCT (Reactant); PREP  
 (Preparation); RACT (Reactant or reagent)  
 (production of dinitrile monomers from olefinic mononitriles by  
 catalytic isomerization and hydrocyanation)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (production of dinitrile monomers from olefinic mononitriles by  
 catalytic isomerization and hydrocyanation)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 19 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2002:888694 CAPLUS [Full-text](#)  
 DOCUMENT NUMBER: 137:371731  
 TITLE: Copper-catalyzed, vapor-phase hydrocyanation process  
 for the conversion of diolefinic compounds with  
 hydrogen cyanide into unsaturated nitriles  
 INVENTOR(S): Druliner, Joe Douglas; Herron, Norman; Lecloux, Daniel  
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA; Harmer, Mark  
 Andrew  
 SOURCE: PCT Int. Appl., 18 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English

10/586490

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2002092551	A2	20021121	WO 2002-US14607	20020510
WO 2002092551	A3	20030213		
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW			
RW:	GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
US 2003045740	A1	20030306	US 2002-140736	20020508
US 6753440	B2	20040622		
CA 2447051	A1	20021121	CA 2002-2447051	20020510
AU 2002308654	A1	20021125	AU 2002-308654	20020510
EP 1395547	A2	20040310	EP 2002-769693	20020510
EP 1395547	B1	20050316		
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR			
TW 580489	B	20040321	TW 2002-91109774	20020510
JP 2004534032	T	20041111	JP 2002-589437	20020510
MX 2003PA10214	A	20040310	MX 2003-PA10214	20031107
PRIORITY APPLN. INFO.:			US 2001-290294P	P 20010511
			WO 2002-US14607	W 20020510

OTHER SOURCE(S): MARPAT 137:371731

AB A catalyzed, vapor-phase process for the hydrocyanation of acyclic diolefinic compds. (e.g., butadiene) to olefinic nitriles (e.g., pentenenitriles) with HCN is described in which the product's olefinic double bond is not conjugated to the triple bond of the cyano group and where a catalyst composition comprising supported copper salts (e.g., cupric triflate/C) is used.

IC ICM C07C253-10  
ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 48, 67

ST butadiene gas phase hydrocyanation pentenenitrile manuf; supported copper catalyst diene hydrocyanation unsatd nitrile manuf

IT Alkadienes  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)

IT Hydrocyanation catalysts  
(supported copper compds. in a vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)

IT Nitriles, preparation  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(unsatd.; copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)

IT 7440-44-0, Activated carbon, uses  
RL: CAT (Catalyst use); USES (Uses)  
(activated, support; copper-compound hydrocyanation catalysts in a vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)

IT 592-51-8P, 4-Pentenenitrile 1647-11-6P, 2-Cyano-1-butene 4635-87-4P, 3-Pentenenitrile

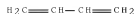
- RL: IMF (Industrial manufacture); PREF (Preparation)  
 (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, Butadiene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)
- IT 34946-82-2, Cupric triflate 42152-44-3, Cuprous triflate  
 RL: CAT (Catalyst use); USES (Uses)  
 (hydrocyanation catalysts in a vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)
- IT 1344-28-1, Alumina, uses 7631-86-9, Silica, uses  
 RL: CAT (Catalyst use); USES (Uses)  
 (support; copper-compound hydrocyanation catalysts in a vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)
- IT 4635-87-4P, 3-Pentenitrile  
 RL: IMF (Industrial manufacture); PREF (Preparation)  
 (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)
- RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, Butadiene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)
- RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



- RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



- IT 1344-28-1, Alumina, uses

RL: CAT (Catalyst use); USES (Uses)  
 (support; copper-compound hydrocyanation catalysts in a  
 vapor-phase hydrocyanation process for the conversion of diolefinic  
 compds. into unsatd. nitriles)

RN 1344-28-1 CAPLUS

CN Aluminum oxide (Al2O3) (CA INDEX NAME)

\*\*\* STRUCTURE DIAGRAM IS NOT AVAILABLE \*\*\*

L88 ANSWER 20 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2002:293580 CAPLUS Full-text

DOCUMENT NUMBER: 136:327370

TITLE: Hydrocyanation method and catalyst systems for  
 converting ethylenically unsaturated organic compounds  
 into nitriles

INVENTOR(S): Burattin, Paolo; Galland, Jean-Christophe; Chamard,  
 Alex

PATENT ASSIGNEE(S): Rhodia Polyamide Intermediates, Fr.

SOURCE: PCT Int. Appl., 24 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: French

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2002030854	A2	20020418	WO 2001-FR3047	20011003
WO 2002030854	A3	20020613		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
FR 2815344	A1	20020419	FR 2000-13152	20001013
FR 2815344	B1	20040130		
TW 584623	B	20040421	TW 2001-90124118	20010928
CA 2425384	A1	20020418	CA 2001-2425384	20011003
AU 2001095653	A	20020422	AU 2001-95653	20011003
EP 1324976	A2	20030709	EP 2001-976353	20011003
EP 1324976	B1	20060201		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR				
BR 2001014807	A	20040106	BR 2001-14807	20011003
HU 2003003560	A2	20040301	HU 2003-3560	20011003
JP 2004511450	T	20040415	JP 2002-534244	20011003
RU 2250896	C2	20050427	RU 2003-113534	20011003
AT 316955	T	20060215	AT 2001-976353	20011003
MX 2003PA03107	A	20040126	MX 2003-PA3107	20030409
US 2004063956	A1	20040401	US 2003-399237	20030924
US 7098358	B2	20060829		

PRIORITY APPLN. INFO.: FR 2000-13152 A 20001013  
 WO 2001-FR3047 W 20011003

OTHER SOURCE(S): MARPAT 136:327370

AB A method for hydrocyanation of ethylenically unsatd. organic compds. into  
 compds. comprising at least a nitrile function comprises the reaction of

hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand with monophosphanorbornadiene structure and the process is particularly useful for the hydrocyanation of butadiene into adiponitrile.

IC ICM C07C

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 29, 67

ST alkene hydrocyanation nitrile prepn; butadiene hydrocyanation isomerization manuf adiponitrile; monophosphanorbornadiene ligand catalyst butadiene hydrocyanation isomerization manuf adiponitrile

IT Nitriles, preparation

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)

(aliphatic; hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT Rare earth halides

RL: CAT (Catalyst use); USES (Uses)

(bromides; in hydrocyanation catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT Nitriles, preparation

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)

(dinitriles, aliphatic; hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT Alkadienes

RL: RCT (Reactant); RACT (Reactant or reagent)

(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT Group IB elements

Group IIB elements

Group IIIA elements

Group IIIB elements

Group IVA elements

Group IVB elements

Group VA elements

Group VB elements

Group VIB elements

Group VIIB elements

Group VIII elements

Lewis acids

Rare earth chlorides

Transition metals, uses

RL: CAT (Catalyst use); USES (Uses)

(in hydrocyanation catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT Phosphines

Phosphites

Phosphoranes

RL: CAT (Catalyst use); USES (Uses)

(monophosphanorbornadienes; in hydrocyanation catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT Nitriles, preparation

RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(unsatd., aliphatic; hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT Alkenes, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

- ( $\alpha$ -; hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 110-59-8P, Valeronitrile 111-69-3P, Adiponitrile 4553-62-2P, 2-Methylglutaronitrile 17611-82-4P  
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
- (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 78-79-5, Isoprene, reactions 106-99-0, Butadiene, reactions 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene  
 RL: PCT (Reactant); PACT (Reactant or reagent)
- (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 592-51-8P, 4-Pentenitrile 4403-61-6P, 2-Methyl-2-butenitrile 4635-87-4E, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
- (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 98-83-9P, Methylstyrene, preparation 100-42-5P, Styrene, preparation 110-83-8P, Cyclohexene, preparation 1335-86-0P, Methylcyclohexene 26588-32-9P, Vinyl naphthalene  
 RL: SPN (Synthetic preparation); PREP (Preparation)
- (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 74-90-8, Hydrogen cyanide, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)
- (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles using)
- IT 815-85-0, Stannous tartrate 1295-35-8, Nickel bis(1,5-cyclooctadiene) 3333-67-3, Nickel carbonate 3349-06-2, Nickel formate 7439-89-6, Iron, uses 7440-05-3, Palladium, uses 7488-55-3, Stannous sulfide 7646-79-9, Cobalt chloride, uses 7646-85-7, Zinc chloride, uses 7699-45-8, Zinc bromide 7718-54-9, Nickel chloride, uses 7758-94-3, Ferrous chloride 7772-99-8, Stannous chloride, uses 7773-01-5, Manganese chloride 7786-81-4, Nickel sulfate 7789-42-6, Cadmium bromide 10031-24-0, Stannous bromide 10108-64-2, Cadmium chloride 10139-47-6, Zinc iodide 10361-92-9, Yttrium chloride 10381-36-9, Nickel phosphate 12054-48-7, Nickel hydroxide 12266-58-9, Nickel bisacrylonitrile 12738-03-3, Manganese bromide 13138-45-9, Nickel nitrate 13462-88-9, Nickel bromide 13462-90-3, Nickel iodide 13689-92-4, Nickel thiocyanate 14220-17-8, Potassium tetracyanonickelate 14332-33-3, Nickel phosphite 15133-82-1, Tetrakis(triphenylphosphine)nickel 16812-54-7, Nickel(II) sulfide 17237-93-3, Nickel bicarbonate 22605-92-1, Nickel citrate 38150-64-0, Cyanic acid, nickel(2+) salt 51142-85-9, Nickel borate 128008-30-0, Indium(III) triflate  
 RL: CAT (Catalyst use); USES (Uses)
- (in hydrocyanation catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 106-99-0, Butadiene, reactions  
 RL: PCT (Reactant); PACT (Reactant or reagent)
- (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4F, 3-Pentenitrile  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP  
 (Preparation); RACT (Reactant or reagent)  
 (hydrocyanation method and catalyst systems for converting  
 ethylenically unsatd. organic compds. into nitriles)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions  
 RL: PCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation method and catalyst systems for converting  
 ethylenically unsatd. organic compds. into nitriles using)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 21 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 2001:228948 CAPLUS Full-text  
 DOCUMENT NUMBER: 134:266726  
 TITLE: Polymeric phosphite catalysts for hydrocyanation of  
 unsaturated organic compounds and isomerization of  
 unsaturated nitriles  
 INVENTOR(S): Tam, Wilson; Kristjansdottir, Sigridur Soley; Greene,  
 Robin Nikolas  
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA  
 SOURCE: PCT Int. Appl., 48 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001021684	A1	20010329	WO 2000-US25568	20000919
W: BR, CA, CN, CZ, ID, JP, KR, MX, PL, SG, SK				
RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
US 6284865	B1	20010904	US 1999-399261	19990920
CA 2384408	A1	20010329	CA 2000-2384408	20000919
BR 2000014478	A	20020618	BR 2000-14478	20000919
EP 1216268	A1	20020626	EP 2000-963590	20000919
EP 1216268	B1	20031112		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,				

IE, FI, CY

CN 1390241	A	20030108	CN 2000-815657	20000919
JP 2003510385	T	20030318	JP 2001-525254	20000919
CN 1847288	A	20061018	CN 2006-10081921	20000919
TW 226345	B	20050111	TW 2000-89119359	20000920
US 2001049431	A1	20011206	US 2001-865942	20010525
US 6855799	B2	20050215		
HK 1052364	A1	20070511	HK 2003-104699	20030702

PRIORITY APPLN. INFO.:

US 1999-399261	A	19990920
CN 2000-815657	A3	20000919
WO 2000-US25568	W	20000919

AB A polymeric composition, a process for producing the composition, and a process for using the composition in, for example, hydrocyanation or isomerization are disclosed. The composition comprises repeat units derived from (1) a carbonyl compound, a monomer, and phosphorochloridite; (2) phosphorus trichloride, a polyhydric alc., and an aromatic diol; or (3) combinations of (1) and (2) in which the monomer can be a polyhydric alc., an amine, combinations thereof. The composition can further comprise a Group VIII metal and optionally a Lewis acid. The composition can be produced by (1) contacting a carbonyl compound with the monomer to produce an intermediate and contacting the intermediate with phosphorochloridite; (2) contacting phosphorus trichloride with a second polyhydric alc. under a condition sufficient to produce a phosphorus-containing polymer and contacting the phosphorus-containing polymer with an aromatic diol; or (3) contacting an N, N-dialkyl dichlorophosphoramidite with a second polyhydric alc. to produce a polymer phosphoramidite, contacting the polymer phosphoramidite with an acid such as HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst, for example, for converting an unsatd. organic compound to a nitrile and isomerizing a nitrile.

IC ICM C08G069-48  
ICS C08G063-91; C08G079-04; B01J031-18

CC 35-5 (Chemistry of Synthetic High Polymers)

ST polyester phosphite hydrocyanation catalyst; polyamide phosphite hydrocyanation catalyst

IT Hydrocyanation catalysts  
Isomerization catalysts  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT Polyamides, preparation  
Polyesters, preparation  
RL: CAT (Catalyst use); IMF (Industrial manufacture); PREP (Preparation); USES (Uses)  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 1295-35-8  
RL: CAT (Catalyst use); USES (Uses)  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 90-02-8DP, Salicylaldehyde, acetals with propanediol, phospho-containing polyesters 504-63-2DP, 1,3-Propanediol, acetals with salicylaldehyde, phospho-containing polyesters 331677-94-2DP, reaction products with o-Cresol phosphorochloridite 331677-99-7P 331722-26-0P  
RL: CAT (Catalyst use); IMF (Industrial manufacture); PREP (Preparation); USES (Uses)  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 4635-87-4P, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)

- (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- IT 331677-94-2P, Dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate-1,6-hexanediol copolymer 331722-22-6P 331722-23-7P 331722-24-8DP, reaction products with o-Cresol phosphorochloridite 331722-24-8P 331722-25-9P
- RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
- (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, Butadiene, reactions 592-51-8, 4-Pentenitrile 818-57-5, Methyl 4-pentenoate 818-58-6, Methyl 3-pentenoate 818-59-7, Methyl 2-pentenoate
- RL: RCT (Reactant); RACT (Reactant or reagent)
- (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- IT 4635-87-4P, 3-Pentenitrile
- RL: IMF (Industrial manufacture); PREP (Preparation)
- (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- RN 4635-87-4 CAPLUS
- CN 3-Pentenitrile (CA INDEX NAME)



- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, Butadiene, reactions
- RL: RCT (Reactant); RACT (Reactant or reagent)
- (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- RN 74-90-8 CAPLUS
- CN Hydrocyanic acid (CA INDEX NAME)



- RN 106-99-0 CAPLUS
- CN 1,3-Butadiene (CA INDEX NAME)



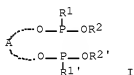
REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 22 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 1999:791822 CAPLUS Full-text

10/586490

DOCUMENT NUMBER: 132:37251  
 TITLE: Group VIII metal complex catalyst with bidentate phosphonite ligand, and method for preparing nitriles  
 INVENTOR(S): Fischer, Jakob; Siegel, Wolfgang; Keitel, Dagmar  
 PASCALE; Siggel, Lorenz  
 PATENT ASSIGNEE(S): BASF A.-G., Germany  
 SOURCE: Ger. Offen., 18 pp.  
 CODEN: GWXXBX  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 19825212	A1	19991209	DE 1998-19825212	19980605
TW 519496	B	20030201	TW 1999-88109210	19990603
CA 2334151	A1	19991216	CA 1999-2334151	19990604
CA 2334151	C	20071023		
WO 9964155	A1	19991216	WO 1999-EP3888	19990604
W: AE, BR, CA, CN, CZ, ID, IN, JP, KR, MX, RU, SG, TR, US				
RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
BR 9910956	A	20010313	BR 1999-10956	19990604
EP 1091804	A1	20010418	EP 1999-927883	19990604
EP 1091804	B1	20020227		
R: BE, DE, ES, FR, GB, IT, NL				
TR 200003625	T2	20010420	TR 2000-3625	19990604
JP 2002517473	T	20020618	JP 2000-553209	19990604
ES 2173750	T3	20021016	ES 1999-927883	19990604
RU 2223146	C2	20040210	RU 2001-101148	19990604
MX 2000PA11522	A	20010521	MX 2000-PA11522	20001123
US 6521778	B1	20030218	US 2000-701601	20001130
IN 2000CN00891	A	20050722	IN 2000-CN891	20050722
PRIORITY APPLN. INFO.:			DE 1998-19825212	A 19980605
			WO 1999-EP3888	W 19990604
OTHER SOURCE(S):	MARPAT 132:37251			
GI				



AB A catalyst useful for the manufacture of mixts. of C5-monoolefinic nitriles with the double bond nonconjugated with nitrile group by hydrocyanation of dienes and for isomerization of branched aliphatic monoalkenenitriles into linear monoalkenenitriles comprises a group VIII metal complex with P-containing ligands (structures specified). A process for the manufacture of adipic acid dinitrile by hydrocyanation of 1,3-butadiene followed by isomerization of the resulting mixture of monoolefinic C5-monoalkenenitriles is also claimed. For example, a mixture of 0.41 g bis(1,5-cyclooctadiene)nickel and 2.14 g ligand I and 10 mL PhMe was placed in a glass autoclave under Ar, stirred for 10 min, a mixture of 7.9 g 1,3-butadiene and 40 g PhMe was added,

the mixture was heated at 70° (pressure increased to 1.2 bar), treated over 90 min with a mixture of 3.2 g HCN and 40 g PhMe (pressure dropped to 0.5 bar) and the whole allowed to react for 120 min at 70° to give a product containing 99.4% of a mixture of MeCH:CHCH2CN (II), CH2:CHCH2CH2CN and CH2:CHCHMeCN (III) with II:III ratio of 0.41:1. II:III ratio can be increased by extending the reaction duration time after HCN addition was completed.

IC ICM B01J031-22

ICS C07F009-40; C07C253-10; C07C255-06; C07C255-04

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

ST Section cross-reference(s): 67

hydrocyanation catalyst alkenenitrile manuf butadiene; butadiene hydrocyanation cyclooctadienenickel complex catalyst phosphonite ligand; hydrocyanic acid hydrocyanation butadiene cyclooctadienenickel complex catalyst phosphonite ligand; methylbutenenitrile manuf cyclooctadienenickel complex catalyst phosphonite ligand; pentenenitrile manuf isomerization cyclooctadienenickel complex catalyst phosphonite ligand

IT Hydrocyanation

Hydrocyanation catalysts

Isomerization

Isomerization catalysts

(group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT Group VIII elements

RL: CAT (Catalyst use); USES (Uses)

(group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT Nitriles, preparation

RL: IMF (Industrial manufacture); PREP (Preparation)

(unsatd., monoolefinic C5-; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 1295-35-8, Bis(1,5-Cyclooctadiene)nickel

RL: CAT (Catalyst use); USES (Uses)

(group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 74-90-8, Hydrocyanic acid, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(hydrocyanation of butadiene; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 106-99-0, 1,3-Butadiene, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(hydrocyanation; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 252253-20-6 252253-21-7

RL: CAT (Catalyst use); USES (Uses)

(ligand; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 4635-87-4E, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile

RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)

(manufacture and isomerization; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 74-90-8, Hydrocyanic acid, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(hydrocyanation of butadiene; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, 1,3-Butadiene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation; group VIII metal complex catalyst with  
 bidentate phosphonite ligand and manufacture of alkenenitriles)  
 RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenitrile  
 RL: IMF (Industrial manufacture); RCT (Reactant); PFEP  
 (Preparation); RACT (Reactant or reagent)  
 (manufacture and isomerization; group VIII metal complex catalyst  
 with bidentate phosphonite ligand and manufacture of alkenenitriles)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



L88 ANSWER 23 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 1998:406229 CAPLUS Full-text  
 DOCUMENT NUMBER: 129:82973  
 TITLE: Monoolefinic C5 mononitrile production and use  
 INVENTOR(S): Siegel, Wolfgang; Munding, Klaus; Meyer, Gerald;  
 Fischer, Jakob  
 PATENT ASSIGNEE(S): BASF A.-G., Germany  
 SOURCE: Ger. Offen., 12 pp.  
 CODEN: GWXXBX  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	----	-----	-----	-----
DE 19652273	A1	19980618	DE 1996-19652273	19961216
CA 2275164	A1	19980625	CA 1997-2275164	19971210
WO 9827054	A1	19980625	WO 1997-EP6900	19971210
W: AL, AU, BG, BR, BY, CA, CN, CZ, GE, HU, ID, IL, JP, KR, KZ, LT, LV, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, UA, US, AM, AZ, KG, MD, TJ, TM				
RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
AU 9858554	A	19980715	AU 1998-58554	19971210

EP 944585	A1	19990929	EP 1997-954375	19971210
EP 944585	B1	20020417		
R: BE, DE, ES, FR, GB, IT, NL				
CN 1245489	A	20000223	CN 1997-181702	19971210
CN 1144781	B	20040407		
BR 9713939	A	20000321	BR 1997-13939	19971210
JP 2001506250	T	20010515	JP 1998-527270	19971210
ES 2175520	T3	20021116	ES 1997-954375	19971210
RU 2217416	C2	20031127	RU 1999-115156	19971210
TW 387874	B	20000421	TW 1997-86118914	19971215
US 6197992	B1	20010306	US 1999-319877	19990614
KR 2000057573	A	20000925	KR 1999-705329	19990615
PRIORITY APPLN. INFO.:			DE 1996-19652273	A 19961216
			WO 1997-EP6900	W 19971210

AB Non-conjugated C5 monoolefinic mononitriles are prepared economically by catalytic hydrocyanation of hydrocarbons containing butadiene (I) from which hydrocyanation poisons have been removed. The continuous reaction of a partially hydrogenated C4 fraction containing I (483 mmol/h) with HCN (414 mmol/h) in the presence of 2.76 mmol/h catalyst containing [(MeC6H4O)3P]4Ni 25, (MeC6H4O)3P 60, and 3-pentenitrile (II)-2-methyl-3-butenitrile (III) 1% at 102-95°/15 bar with residence time 80 min gave HCN conversion >99.8%, selectivity vs. I 98%, II-III ratio 2.0:1, and active Ni recovery 90.0%; vs. 98.0, 97, 1.95:1, and 61.3, resp., when a non-hydrogenated C4 fraction was used.

IC ICM C07C255-07  
ICS C07C253-10; C07C255-04; C07B035-02

ICA B01J031-22

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23

IT 106-99-0, Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation in purified C4 fractions)

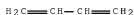
IT 4635-87-4E, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(monoolefinic C5 mononitrile production and use)

IT 74-90-8, Hydrocyanic acid, reactions  
RL: PCT (Reactant); RACT (Reactant or reagent)  
(reaction with butadiene)

IT 106-99-0, Butadiene, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation in purified C4 fractions)

RN 106-99-0 CAPLUS

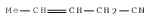
CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenitrile  
RL: IMF (Industrial manufacture); PREP (Preparation)  
(monoolefinic C5 mononitrile production and use)

RN 4635-87-4 CAPLUS

CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrocyanic acid, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction with butadiene)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 24 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 1997:679045 CAPLUS Full-text  
 DOCUMENT NUMBER: 127:308629  
 TITLE: Catalyzed vapor-phase hydrocyanation of diolefinic compounds  
 INVENTOR(S): Druliner, Joe Douglas; Herron, Norman  
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA; Druliner, Joe Douglas; Herron, Norman  
 SOURCE: PCT Int. Appl., 19 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9736855	A2	19971009	WO 1997-US4903	19970327
WO 9736855	A3	19971106		
W: BR, CA, CN, JP, KR, SG, US, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
IN 191521	A1	20031206	IN 1997-CA492	19970319
TW 458959	B	20011011	TW 1997-86103681	19970324
EP 891323	A2	19990120	EP 1997-917016	19970327
EP 891323	B1	20060614		
R: DK, FR, GB, IT, NL				
EP 1621531	A1	20060201	EP 2005-77325	19970327
EP 1621531	B1	20070314		
R: FR, GB, IT, NL				
PRIORITY APPLN. INFO.:			US 1996-14618P	P 19960402
			EP 1997-917016	A3 19970327
			WO 1997-US4903	W 19970327

OTHER SOURCE(S): MARPAT 127:308629

AB A catalyzed vapor-phase process for the hydrocyanation of acyclic diolefinic compds. to olefinic nitriles comprises reacting an acyclic diolefinic compound with HCN in the vapor-phase at temperature 135-300° in the presence of a supported catalyst composition comprising at least one multidentate phosphite ligand, zero-valent nickel, and specially selected or treated supports.  
 IC ICM C07C253-10  
 CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
 Section cross-reference(s): 23  
 ST hydrocyanation diene vapor phase; catalyst hydrocyanation olefin nickel



- phosphite supported  
 IT Hydrocyanation  
 Hydrocyanation catalysts  
 (catalyzed vapor-phase hydrocyanation of diolefinic compds.)  
 IT 11063-09-5 180974-36-1  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalyzed vapor-phase hydrocyanation of diolefinic compds.)  
 IT 169254-14-2P 169254-15-3P  
 RL: CAT (Catalyst use); IMF (Industrial manufacture); PREP (Preparation);  
 USES (Uses)  
 (catalyzed vapor-phase hydrocyanation of diolefinic compds.)  
 IT 592-51-8P, 4-Pentenitrile 4635-87-4P, 3-Pentenitrile  
 RL: IMF (Industrial manufacture); PREP (Preparation)  
 (catalyzed vapor-phase hydrocyanation of diolefinic compds.)  
 IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions 6108-61-8 108032-25-3, trans-2,4-Hexadiene  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (catalyzed vapor-phase hydrocyanation of diolefinic compds.)  
 IT 9003-53-6, Polystyrene  
 RL: CAT (Catalyst use); USES (Uses)  
 (crosslinked, support; catalyzed vapor-phase hydrocyanation  
 of diolefinic compds.)  
 IT 7440-44-0, Carbon, uses  
 RL: CAT (Catalyst use); USES (Uses)  
 (heat-treated, support; catalyzed vapor-phase hydrocyanation  
 of diolefinic compds.)  
 IT 1344-28-1, Alumina, uses 7631-86-9, Silica, uses  
 9003-69-4, Divinylbenzene homopolymer 9058-15-5, Chromosorb 104  
 25014-41-9, Polyacrylonitrile  
 RL: CAT (Catalyst use); USES (Uses)  
 (support; catalyzed vapor-phase hydrocyanation of diolefinic  
 compds.)  
 IT 4635-87-4P, 3-Pentenitrile  
 RL: IMF (Industrial manufacture); PREP (Preparation)  
 (catalyzed vapor-phase hydrocyanation of diolefinic compds.)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (catalyzed vapor-phase hydrocyanation of diolefinic compds.)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



- RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)

$$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$$

IT 1344-28-1, Alumina, uses  
 RL: CAT (Catalyst use); USES (Uses)  
 (support; catalyzed vapor-phase hydrocyanation of diolefinic  
 compds.)  
 RN 1344-28-1 CAPLUS  
 CN Aluminum oxide (Al2O3) (CA INDEX NAME)

\*\*\* STRUCTURE DIAGRAM IS NOT AVAILABLE \*\*\*

L88 ANSWER 25 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1991:412659 CAPLUS Full-text

DOCUMENT NUMBER: 115:12659

TITLE: Plasma discharge in nitrogen + methane at low  
 pressures: experimental results and applications to  
 Titan

AUTHOR(S): Thompson, W. Reid; Henry, Todd J.; Schwartz, Joel M.;  
 Khare, B. N.; Sagan, Carl

CORPORATE SOURCE: Lab. Planet. Stud., Cornell Univ., Ithaca, NY, 14853,  
 USA

SOURCE: Icarus (1991), 90(1), 57-73  
 CODEN: ICRSA5; ISSN: 0019-1035

DOCUMENT TYPE: Journal

LANGUAGE: English

AB The yields of gaseous hydrocarbons and nitriles produced in a continuous flow, low-dose, cold plasma discharge excited in a 10% CH<sub>4</sub>, 90% N<sub>2</sub> atmospheric at 295 K and pressures (P) of 17 and 0.24 mbar are determined; the results are used to compute expected abundances of minor constituents in Titan's atmospheric. These expts. are, by design, relevant to the atmospheric chemical induced by cosmic rays in Titan's troposphere and (at the lower P) to chemical initiated by Saturnian magnetospheric electrons and other charged particle sources which excite stratospheric auroras. At P = 17 mbar, 59 gaseous species including 27 nitriles are detected in overall yield 4.0 (C + N) atoms incorporated into products per 100 eV (heV). At P = 0.24 mbar, 19 species are detected, including 6 nitriles and 3 other unidentified N-bearing compds.; the yield is 0.79 (C + N)/heV, a mild decrease with P. The types of mols. formed change more markedly, with high degrees of multiple bonding at 0.24 mbar prevailing over more H-saturated mols. at 17 mbar. The mols. and yields at 0.24 mbar bear a striking resemblance to the minor constituents found in Titan's atmospheric, all of which are abundant products in the laboratory experiment. Using the altitude-integrated flux of charged particle energy deposition at Titan, the laboratory yields at P = 0.24 mbar, and a simple eddy mixing model, absolute stratospheric column abundances and mole fractions were computed. These are in very good agreement with the Voyager IRIS observations. Except for the primarily photochem. products, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>, the match is much better than that obtained by photochem.-kinetic models, demonstrating that properly designed laboratory expts. are directly applicable to modeling radiation-chemical processes in planetary atmospheres. On the basis of this agreement; CH<sub>3</sub>-C.tplbond.N (ethanenitrile = acetonitrile) CH<sub>2</sub>:CH-CH:CH<sub>2</sub> (1,3-butadiene), CH<sub>2</sub>:C:CH<sub>2</sub> (1,2-propadiene = allene), and CH<sub>2</sub>:CH-C.tplbond.CH (1-buten-3-yne) to be present at mol fractions X > 10<sup>-9</sup>, and CH<sub>2</sub>:CH-C.tplbond.N (propenenitrile), CH<sub>3</sub>-CH:CH<sub>2</sub> (propene), and CH<sub>3</sub>-CH<sub>2</sub>-C.tplbond.N (propanenitrile) at X > 10<sup>-10</sup> are expected in Titan's atmospheric  
 CC 53-9 (Mineralogical and Geological Chemistry)

- IT 74-84-0P, Ethane, preparation 74-85-1P, Ethene, preparation 74-86-2P, Ethyne, preparation 74-90-8P, Hydrocyanic acid, preparation 74-98-6P, Propane, preparation 74-99-7P, 1-Propyne 75-05-8P, Ethanenitrile, preparation 75-19-4P, Cyclopropane 75-28-5P 75-83-2P, 2,2-Dimethylbutane 78-78-4P, 2-Methylbutane 78-82-0P, 2-Methylpropanenitrile 106-97-8P, Butane, preparation 106-98-9P, 1-Butene, preparation 106-99-0P, 1,3-Butadiene, preparation 107-00-6P, 1-Butyne 107-12-0P, Propanenitrile 107-13-1P, 2-Propenenitrile, preparation 107-83-5P, 2-Methylpentane 109-66-0P, Pentane, preparation 109-67-1P, 1-Pentene 109-74-0P, Butanenitrile 109-75-1P, 3-Butenenitrile 115-07-1P, Propene, preparation 115-11-7P, 2-Methylpropene, preparation 126-98-7P, 2-Methyl-2-propenenitrile 287-23-0P, Cyclobutane 290-96-0P, 1,2,4,5-Tetrazine 460-12-8P, 1,3-Butadiyne 460-19-5P, Ethanedinitrile 463-49-0P, Propadiene 463-82-1P, 2,2-Dimethylpropane 503-17-3P, 2-Butyne 513-35-9P, 2-Methyl-2-butene 542-92-7P, 1,3-Cyclopentadiene, preparation 563-45-1P, 3-Methyl-1-butene 563-46-2P, 2-Methyl-1-butene 590-18-1P, cis-2-Butene 590-19-2P, 1,2-Butadiene 592-51-8P, 4-Pentenitrile 624-64-6P, trans-2-Butene 627-20-3P, cis-2-Pentene 627-26-9P, trans-2-Butenenitrile 630-18-2P, 2,2-Dimethylpropanenitrile 646-04-8P, trans-2-Pentene 689-97-4P, 1-Buten-3-yne 1070-71-9P, Propynenitrile 1190-76-7P, cis-2-Butenenitrile 1516-01-4P, 2,4-Hexadienenitrile 1615-70-9P, 2,4-Pentadienenitrile 4786-19-0P, 3-Methyl-3-butenenitrile 5167-62-4P 13752-78-8P, 2-Butynenitrile 16529-66-9P, 2-Methyl-3-butenenitrile 16529-66-1P, trans-3-Pentenitrile 17761-23-8P 20068-02-4P 25899-50-7P, cis-2-Pentenitrile 26294-98-4P, trans-2-Pentenitrile 30574-97-1P
- RL: GFM (Geological or astronomical formation); FORM (Formation, nonpreparative); PREP (Preparation)
- (formation of, continuous flow plasma discharge irradiation of nitrogen- and methane-containing atmospheric in relation to)
- IT 74-82-8, Methane, occurrence 7727-37-9, Nitrogen, occurrence
- RL: OCCU (Occurrence)
- (in Titan's atmospheric, plasma discharge in, exptl. study in relation to)
- IT 74-90-8P, Hydrocyanic acid, preparation 106-99-0P, 1,3-Butadiene, preparation 16529-66-1P, trans-3-Pentenitrile
- RL: GFM (Geological or astronomical formation); FORM (Formation, nonpreparative); PREP (Preparation)
- (formation of, continuous flow plasma discharge irradiation of nitrogen- and methane-containing atmospheric in relation to)
- RN 74-90-8 CAPLUS
- CN Hydrocyanic acid (CA INDEX NAME)



- RN 106-99-0 CAPLUS
- CN 1,3-Butadiene (CA INDEX NAME)

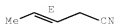


- RN 16529-66-1 CAPLUS

10/586490

CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



IT 7727-37-9, Nitrogen, occurrence

RL: OCCU (Occurrence)

(in Titan's atmospheric, plasma discharge in, exptl. study in relation to)

RN 7727-37-9 CAPLUS

CN Nitrogen (CA INDEX NAME)



L88 ANSWER 26 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1984:50763 CAPLUS Full-text

DOCUMENT NUMBER: 100:50763

ORIGINAL REFERENCE NO.: 100:7757a,7760a

TITLE: Catalytic hydrocyanation of olefins by nickel(0)

phosphite complexes - effects of Lewis acids

AUTHOR(S): Tolman, C. A.; Seidel, W. C.; Druliner, J. D.;

Domaille, P. J.

CORPORATE SOURCE: Cent. Res. Dev. Dep., E. I. du Pont de Nemours and

Co., Wilmington, DE, 19898, USA

SOURCE: Organometallics (1984), 3(1), 33-8

CODEN: ORGND7; ISSN: 0276-7333

DOCUMENT TYPE: Journal

LANGUAGE: English

AB In this abstract L = (o-MeC<sub>6</sub>H<sub>4</sub>O)3P (I) or (p-MeC<sub>6</sub>H<sub>4</sub>O)3P (II). Mechanistic studies on the addition of HCN to olefins using Ni<sup>3I</sup> catalyst show that the reactions proceed under mild conditions via (η<sup>1</sup>-organo)- or (η<sup>3</sup>-organo)nickel cyanide intermediates, formed by the insertion of monoenes or dienes into the Ni-H bond of L<sub>3</sub>NiHCN. The RNiLmCN intermediates are identified by NMR and IR in some cases. In the case of very electroneg. R groups (formed for example from reactions of L<sub>3</sub>NiHCN with C<sub>2</sub>F<sub>4</sub> or CH<sub>2</sub>:CHCN), reductive elimination does not occur, and the catalyst is poisoned for olefin hydrocyanation. Improved rates, catalyst lifetimes, and product linearity are obtained by the addition of Lewis acid (Q) cocatalysts. Spectroscopic studies show that Lewis acids coordinate strongly to the N atom lone-electron pair of hydrido cyanide intermediates to form L<sub>3</sub>NiHCN·Q. The effects of Lewis acids on hydrocyanation involves increasing the concentration of Ni in catalytic loop species (in the II system), accelerating the rate of C-C coupling to form alkanenitriles from alkylnickel cyanide complexes, and destabilizing relatively bulky branched alkyl intermediates relative to less crowded linear ones.

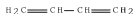
CC 22-4 (Physical Organic Chemistry)

Section cross-reference(s): 29

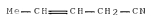
ST mechanism alkene hydrocyanation; kinetics alkene hydrocyanation; nickel phosphite complex hydrocyanation catalyst; Lewis acid hydrocyanation catalyst

IT Alkenes, reactions

- RL: RCT (Reactant); RACT (Reactant or reagent)  
(catalytic hydrocyanation of, Lewis acid effects and mechanism of)
- IT Lewis acids  
RL: PRP (Properties)  
(effect of, on hydrocyanation of alkenes catalyzed by nickel phosphite complexes)
- IT Hydrocyanation catalysts  
(nickel phosphite complexes, for alkenes, effect of Lewis acids in relation to mechanism with)
- IT Regiochemistry  
(of catalytic hydrocyanation of alkenes by nickel phosphite complexes)
- IT Steric effect  
Substituent effect  
(on catalytic hydrocyanation of alkenes)
- IT Addition reaction  
(oxidative, in catalytic hydrocyanation of alkenes)
- IT 960-71-4 1088-01-3 1095-03-0 7446-70-0, uses and miscellaneous  
7646-85-7, uses and miscellaneous 42270-57-5  
RL: PRP (Properties)  
(effect of, on nickel phosphite complex catalyzed hydrocyanation of olefins)
- IT 28829-00-7 87482-65-3  
RL: CAT (Catalyst use); USES (Uses)  
(hydrocyanation catalyst, for alkenes, mechanism with)
- IT 106-99-0, reactions 115-07-1, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation of, mechanism of nickel phosphite catalyzed)
- IT 100-42-5, reactions 558-37-2 592-42-7 592-48-3 592-51-8  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation of, mechanism of nickel phosphite complex catalyzed)
- IT 107-12-0P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(preparation of, from hydrocyanation of ethylene, mechanism of catalytic)
- IT 87482-64-2P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(preparation of, in catalytic hydrocyanation of hexadienes)
- IT 17611-82-4P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(preparation of, in catalytic hydrocyanation of pentenenitrile)
- IT 4635-87-4P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(preparation, double bond isomerization, and hydrocyanation of, mechanism of)
- IT 74-90-8, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(reaction of, with nickel phosphite complex)
- IT 106-99-0, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation of, mechanism of nickel phosphite catalyzed)
- RN 106-99-0 CAPLUS
- CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation, double bond isomerization, and hydrocyanation of, mechanism of)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with nickel phosphite complex)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 27 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1984:490011 CAPLUS Full-text  
 DOCUMENT NUMBER: 101:90011  
 ORIGINAL REFERENCE NO.: 101:13795a,13798a  
 TITLE: Homogeneous nickel-catalyzed olefin hydrocyanation  
 AUTHOR(S): Seidel, W. C.; Tolman, C. A.  
 CORPORATE SOURCE: E. I. du Pont de Nemours and Co., Wilmington, DE, 19898, USA  
 SOURCE: Annals of the New York Academy of Sciences (1983), 415(Catal. Transition Met. Hydrides), 201-21  
 CODEN: ANYAA9; ISSN: 0077-8923

DOCUMENT TYPE: Journal  
 LANGUAGE: English

AB Olefin hydrocyanation follows the 16- and 18-electron rule. Activated olefins like  $\text{CH}_2=\text{CH}_2$  or  $\text{CH}_2=\text{CHCH}=\text{CH}_2$  add HCN without Lewis acids at high rates to give good yields of nitriles. Unactivated olefins (e.g., 4-pentenitrile) require both Lewis acids and Ni(0) complexes for efficient linear hydrocyanation. The kinetics and mechanisms of these reactions are discussed.

CC 22-4 (Physical Organic Chemistry)

ST hydrocyanation alkene kinetics mechanism; nickel hydrocyanation catalyst homogeneous

IT Alkenes, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation of, kinetics and mechanism of homogeneous nickel catalyzed)

IT Hydrocyanation catalysts  
 (nickel phosphines, for alkenes, kinetics and mechanism with)

IT Kinetics of hydrocyanation  
 (of alkenes in presence of nickel-phosphine catalyst)

IT 960-71-4 1088-01-3 1095-03-0 42270-57-5  
 RL: RCT (Reactant); RACT (Reactant or reagent)

(effect of, on nickel-phosphine complex catalyzed  
hydrocyanation of olefins)

IT 74-90-8, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation by, nickel phosphine complexes as catalysts  
for)

IT 74-85-1, reactions 107-13-1, reactions 109-75-1 592-41-6, reactions  
592-51-8 5048-19-1 16529-66-1 25899-50-7 26294-98-4

RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation of, equilibrium for nickel complex catalyzed)

IT 106-99-0, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation of, mechanism of nickel complex catalyzed)

IT 4635-87-4P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP  
(Preparation); RACT (Reactant or reagent)  
(preparation and hydrocyanation of)

IT 74-90-8, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation by, nickel phosphine complexes as catalysts  
for)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)

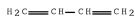


IT 106-99-0, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydrocyanation of, mechanism of nickel complex catalyzed)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP  
(Preparation); RACT (Reactant or reagent)  
(preparation and hydrocyanation of)

RN 4635-87-4 CAPLUS

CN 3-Pentenitrile (CA INDEX NAME)



10/586490

DOCUMENT NUMBER: 83:58183  
 ORIGINAL REFERENCE NO.: 83:9163a,9166a  
 TITLE: Organic nitriles  
 INVENTOR(S): Waddan, Dhafir Y.; Crooks, Graham R.  
 PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd., UK  
 SOURCE: Ger. Offen., 17 pp.  
 CODEN: GWXXBX  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2450863	A1	19750507	DE 1974-2450863	19741025
GB 1482909	A	19770817	GB 1973-50604	19741007
US 3947487	A	19760330	US 1974-514315	19741011
BE 821270	A1	19750418	BE 1974-149706	19741018
JP 50071626	A	19750613	JP 1974-124213	19741028
JP 58002231	B	19830114		
NL 7414172	A	19750502	NL 1974-14172	19741030
FR 2249874	A1	19750530	FR 1974-36272	19741030

PRIORITY APPLN. INFO.:  
 GB 1973-50604 A 19731031  
 GB 1974-2194 A 19740117

AB Organic sulfides [e.g., Pr<sub>2</sub>S, (PhCH<sub>2</sub>)<sub>2</sub>S] and CuCl or CuBr were used as catalysts for addition of HCN to butadiene or isoprene. Thus, heating 19.5 g butadiene, 15 ml HCN, and 1.8 g CuCl in 3 ml thiophene 17 hr at 120° (sealed tube) gave 91.6% 3-pentenitrile and 8.4% 2-methyl-3-butenitrile.

IC C07C

CC 23-19 (Aliphatic Compounds)

ST addn hydrocyanic acid diene catalyst; olefinic aliph nitrile; butadiene hydrocyanic acid addn catalyst; isoprene hydrocyanic acid addn catalyst

IT Addition reaction catalysts  
 (cuprous halides-organic sulfides for butadiene and isoprene with hydrocyanic acid)

IT 74-90-6  
 RL: PCT (Reactant); PACT (Reactant or reagent)  
 (addition reaction of, with butadiene and isoprene, catalysts for)

IT 78-79-5, reactions 106-99-0, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (addition reaction of, with hydrocyanic acid, catalysts for)

IT 75-18-3 108-98-5 110-02-1 111-48-8 139-66-2 352-93-2 544-02-5  
 7787-70-4  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts, for addition reaction of butadiene with hydrocyanic acid)

IT 111-47-7 538-74-9 7758-89-6  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts, for addition reaction of hydrocyanic acid with butadiene and isoprene)

IT 4635-87-4F 16529-56-9P  
 RL: PREP (Preparation)  
 (from butadiene by reaction with hydrocyanic acid, catalysts for)

IT 4786-23-6P  
 RL: PREP (Preparation)  
 (from isoprene by reaction with hydrocyanic acid, catalysts for)

IT 74-90-8



10/586490

RL: RCT (Reactant); RACT (Reactant or reagent)  
(addition reaction of, with butadiene and isoprene, catalysts  
for)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)  
(addition reaction of, with hydrocyanic acid, catalysts for)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P

RL: PREP (Preparation)  
(from butadiene by reaction with hydrocyanic acid, catalysts  
for)

RN 4635-87-4 CAPLUS

CN 3-Pentenitrile (CA INDEX NAME)



L88 ANSWER 29 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1975:97704 CAPLUS Full-text

DOCUMENT NUMBER: 82:97704

ORIGINAL REFERENCE NO.: 82:15593a,15596a

TITLE: Hydrocyanation of conjugated diolefins

INVENTOR(S): Seidel, William C.; Tolman, Chadwick A.

PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co.

SOURCE: U.S., 3 pp.  
CODEN: USXXAM

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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US 3850973	A	19741126	US 1973-401072	19730926
BE 820308	A1	19750325	BE 1974-148862	19740925
DE 2445731	A1	19750403	DE 1974-2445731	19740925
FR 2244753	A1	19750418	FR 1974-32324	19740925

10/586490

FR 2244753 B1 19790202  
 JP 50059326 A 19750522 JP 1974-109629 19740925  
 JP 58042183 B 19830917  
 GB 1436932 A 19760526 GB 1974-41704 19740925  
 PRIORITY APPLN. INFO.: US 1973-401072 A 19730926  
 AB HCN reacted with H2C:CHCH:CH2 at -50 to +150° in the presence of Ni[P-(OC6H4Me-4)3]3 (NCCH2CH:CHMe)3 to give a 2:1 mixture of NCCH2CH:CHMe and NCCHMeCH:CH2.  
 IC C07C  
 INCL 260464000  
 CC 23-19 (Aliphatic Compounds)  
 IT Hydrocyanation catalysts  
 (nickel  $\pi$ -allyl complexes, for dienes)  
 IT 54637-55-7 54637-56-8  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts, for diene hydrocyanation)  
 IT 106-99-0, reactions 542-92-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation of, catalysts for)  
 IT 3047-38-9P 4492-41-5P 4635-87-4P 16529-56-9P 26555-56-6P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)  
 IT 74-90-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with dienes)  
 IT 106-99-0, reactions  
 RL: PCT (Reactant); RACT (Reactant or reagent)  
 (hydrocyanation of, catalysts for)  
 RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8  
 RL: PCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with dienes)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 30 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 1974:145481 CAPLUS Full-text  
 DOCUMENT NUMBER: 80:145481  
 ORIGINAL REFERENCE NO.: 80:23477a,23480a  
 TITLE: 3-Pentenitrile  
 INVENTOR(S): Waddan, Dhafir Y.  
 PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd.  
 SOURCE: Ger. Offen., 11 pp.  
 CODEN: GWXXBX  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2344767	A1	19740314	DE 1973-2344767	19730905
GB 1429169	A	19760324	GB 1972-41487	19730821
US 3869501	A	19750304	US 1973-392008	19730827
BE 804557	A1	19740306	BE 1973-135401	19730906
FR 2198932	A1	19740405	FR 1973-32127	19730906
IT 998546	B	19760220	IT 1973-28647	19730906
JP 49092022	A	19740903	JP 1973-100388	19730907
PRIORITY APPLN. INFO.:			GB 1972-41487	A 19720907

AB MeCH:CHCH2CN was prepared in ≤88.8% yield by reaction of CH2:CHCH:CH2 with HCN in the presence of CuCl in organic acids, e.g. AcOH.  
 IC C07C  
 CC 23-19 (Aliphatic Compounds)  
 ST pentenenitrile; copper chloride catalyst  
 IT Addition reaction catalysts  
 (copper chloride, for hydrocyanic acid to butadiene)  
 IT 7758-89-6  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts, in hydrocyanic acid addition to butadiene)  
 IT 4635-87-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)  
 IT 74-90-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with butadiene)  
 IT 106-59-0, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (with hydrocyanic acid)  
 IT 4635-87-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



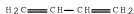
IT 74-90-8

10/586490

RL: RCT (Reactant); RACT (Reactant or reagent)  
(reaction of, with butadiene)  
RN 74-90-8 CAPLUS  
CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(with hydrocyanic acid)  
RN 106-99-0 CAPLUS  
CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 31 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 1974:120342 CAPLUS Full-text  
DOCUMENT NUMBER: 80:120342  
ORIGINAL REFERENCE NO.: 80:19367a,19370a  
TITLE: 3-Pentenitrile  
INVENTOR(S): Waddan, Dhafir Y.  
PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd.  
SOURCE: Ger. Offen., 13 pp.  
CODEN: GWXXBX  
DOCUMENT TYPE: Patent  
LANGUAGE: German  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2336852	A1	19740214	DE 1973-2336852	19730719
DE 2336852	C2	19841004		
GB 1429651	A	19760324	GB 1972-35639	19730705
US 3849472	A	19741119	US 1973-377183	19730709
BE 802730	A1	19740124	BE 1973-133817	19730724
IT 995062	B	19751110	IT 1973-27010	19730724
NL 7310509	A	19740204	NL 1973-10509	19730730
FR 2194691	A1	19740301	FR 1973-27817	19730730
JP 49092020	A	19740903	JP 1973-85514	19730731
JP 57026267	B	19820603		

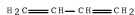
PRIORITY APPLN. INFO.: GB 1972-35639 A 19720731  
AB 3-Pentenitrile (I), useful for the manufacture of adiponitrile, was prepared by reaction of CH<sub>2</sub>:CHCH:CH<sub>2</sub> (II) with HCN in the presence of a complex of CuCl with an organic nitrile, e.g. (NC)2C:C(CN)2 (III) and MeCN. Thus, II and HCN were added to CuCl, III, and MeCN at -20° and the mixture heated 60 hr at 100° in a closed vessel to give 88.3% I.  
IC C07C  
CC 23-19 (Aliphatic Compounds)

10/586490

ST pentenenitrile; butadiene hydrocyanation catalyst; copper complex hydrocyanation catalyst; nitrile complex hydrocyanation catalyst  
 IT Nitriles, uses and miscellaneous  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts, with cuprous chloride, for hydrocyanation of butadiene)  
 IT Hydrocyanation catalysts  
 (cuprous chloride, containing organic nitriles, for butadiene)  
 IT 4635-87-4P  
 RL: PPEP (Preparation)  
 (by hydrocyanation of butadiene)  
 IT 75-05-8, uses and miscellaneous 107-13-1, uses and miscellaneous 670-54-2, uses and miscellaneous  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts, containing cuprous chloride, for hydrocyanation of butadiene)  
 IT 7758-89-6  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts, containing organic nitriles, for hydrocyanation of butadiene)  
 IT 106-99-0, reactions  
 RL: PCT (Reactant); PACT (Reactant or reagent)  
 (hydrocyanation of, catalysts for)  
 IT 74-90-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with butadiene, catalysts for)  
 IT 4635-87-4P  
 RL: PREP (Preparation)  
 (by hydrocyanation of butadiene)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 106-99-0, reactions  
 RL: PCT (Reactant); PACT (Reactant or reagent)  
 (hydrocyanation of, catalysts for)  
 RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



IT 74-90-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with butadiene, catalysts for)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 32 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 1973:135702 CAPLUS Full-text  
 DOCUMENT NUMBER: 78:135702  
 ORIGINAL REFERENCE NO.: 78:21789a,21792a  
 TITLE: Unsaturated nitriles  
 INVENTOR(S): Albanese, Pietro; Benzoni, Luigi; Carnisio, Giuseppe;  
 Colombo, Luigi  
 PATENT ASSIGNEE(S): Montecatini Edison S.p.A.  
 SOURCE: Ital., 10 pp.  
 CODEN: ITXXAX  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Italian  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
	IT 869902		19700819	IT	19690812
AB	Butadiene reacts with HCN in the presence of Fe(CO)5-Ph2P(CH2) PPh2 reaction products (n = 0-12) to give CH2:CHCHMeCN, MeCH:CHCH2CN, trans-MeCH:CMcCN, and 3-vinylcyclohexene. The diphosphine-Fe(CO)5 molar ratio is 1-10:1.				
IC	C07C				
CC	23-19 (Aliphatic Compounds)				
ST	butadiene addn hydrogen cyanide; iron carbonyl addn reaction catalyst; diphosphine deriv addn reaction catalyst; pentenonitrile prepn; butenonitrile methyl; methylbutenonitrile prepn				
IT	Addition reaction catalysts (diphosphine-iron pentacarbonyl complexes, for butadiene with hydrocyanic acid)				
IT	74-90-8				
	RL: RCT (Reactant); RACT (Reactant or reagent) (addition reaction with butadiene, catalysts for)				
IT	106-99-0, reactions				
	RL: RCT (Reactant); RACT (Reactant or reagent) (addition reaction with hydrocyanic acid, catalysts for)				
IT	1101-41-3 7688-25-7		19845-69-3	27721-02-4 27721-03-5	41625-30-3
	41625-32-5				
	RL: CAT (Catalyst use); USES (Uses) (catalyst, for addition of hydrocyanic acid to butadiene)				
IT	766-03-0P 4635-87-4P		16529-56-9P	30574-97-1P	
	RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of)				
IT	74-90-8				
	RL: RCT (Reactant); RACT (Reactant or reagent) (addition reaction with butadiene, catalysts for)				
RN	74-90-8 CAPLUS				
CN	Hydrocyanic acid (CA INDEX NAME)				



IT 196-99-0, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (addition reaction with hydrocyanic acid, catalysts for)  
 RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)  
 RN 4635-87-4 CAPLUS  
 CN 3-Pentenitrile (CA INDEX NAME)



L88 ANSWER 33 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1973:135701 CAPLUS [Full-text](#)  
 DOCUMENT NUMBER: 78:135701  
 ORIGINAL REFERENCE NO.: 78:21789a, 21792a  
 TITLE: Unsaturated nitriles  
 INVENTOR(S): Albanese, Pietro; Benzoni, Luigi; Carnisio, Giuseppe;  
 Crivelli, Armando  
 PATENT ASSIGNEE(S): Montecatini Edison S.p.A.  
 SOURCE: Ital., 15 pp.  
 CODEN: ITXXAX  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Italian  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
	IT 869900		19700819	IT	19690812
AB	Mixts. of $\text{CH}_2\text{:CHCHMeCN}$ , $\text{MeCH:CHCH}_2\text{CN}$ , $\text{EtCH:CHCN}$ , and cis- and trans- $\text{MeCH:CMechCN}$ are obtained by the addition of HCN to butadiene in the presence of reaction products of $\text{Ni(CO)}_4$ and $\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2$ (I) (n is an integer of 0-12). The I- $\text{Ni(CO)}_4$ molar ratio is 1:1-10:1, the $\text{HCN-Ni(CO)}_4$ molar ratio is 10:1-100:1, and the reaction temperature is 50-200°.				
IC	C07C				
CC	23-19 (Aliphatic Compounds)				
ST	butadiene hydrogen cyanide addn; addn reaction catalyst diphosphine; diphosphine nickel carbonyl catalyst; pentenitrile prepn; methylbutenenitrile prepn; butenenitrile methyl				
IT	Addition reaction catalysts (diphosphine-nickel tetracarbonyl reaction products, for hydrocyanic acid with butadiene)				
IT	74-90-3 RL: PCT (Reactant); PACT (Reactant or reagent)				

(addition reaction with butadiene, catalysts for)

IT 106-99-0, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (addition reaction with hydrocyanic acid, catalysts for)

IT 1663-45-2D, Phosphine, 1,2-ethanediylbis(diphenyl-, nickel complexes 19845-69-3D,  
 2071-20-7D, Phosphine, methylenebis(diphenyl-, nickel complexes 27721-02-4D,  
 6737-42-4D, Phosphine, 1,3-propanediylbis(diphenyl-, nickel complexes 27721-03-5D,  
 7688-25-7D, Phosphine, 1,4-butanediylbis(diphenyl-, nickel complexes 41625-30-3D,  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalyst, for addition reaction of hydrocyanic acid with  
 butadiene)

IT 1101-41-3D, Diphosphine, tetraphenyl-, nickel complexes 19845-69-3D,  
 Phosphine, 1,6-hexanediylbis(diphenyl-, nickel complexes 27721-02-4D,  
 Phosphine, 1,5-pentanediylbis(diphenyl-, nickel complexes 27721-03-5D,  
 Phosphine, 1,10-decanediylbis(diphenyl-, nickel complexes 41625-30-3D,  
 Phosphine, 1,8-octanediylbis(diphenyl-, nickel complexes 41625-32-5D,  
 Phosphine, 1,12-dodecanediylbis(diphenyl-, nickel complexes  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalyst, for hydrocyanic acid addition reaction with  
 butadiene)

IT 4635-87-4P 16529-56-9P 16529-66-1P 20068-02-4P  
 25899-50-7P 30574-97-1P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)

IT 74-90-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (addition reaction with butadiene, catalysts for)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (addition reaction with hydrocyanic acid, catalysts for)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P 16529-56-9P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)

RN 4635-87-4 CAPLUS

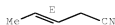
CN 3-Pentenitrile (CA INDEX NAME)





RN 16529-66-1 CAPLUS  
 CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



L88 ANSWER 34 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 1949:22671 CAPLUS Full-text  
 DOCUMENT NUMBER: 43:22671  
 ORIGINAL REFERENCE NO.: 43:4286b-c  
 TITLE: Unsaturated nitriles  
 INVENTOR(S): Schulze, Walter A.; Mahan, John E.  
 PATENT ASSIGNEE(S): Phillips Petroleum Co.  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Unavailable  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	US 2464723		19490315	US 1944-563744	19441116
AB	A liquid stream of a conjugated diolefin and HCN in a mol. ratio between 2:1 and 1.25:1, with MeCN as a diluent, is passed over a solid porous anhydrous CuCl catalyst at 100-350°F. and at a pressure of 100-700 lb./sq. in. An unsatd. nitrile is recovered from the effluent stream; e.g., butadiene and HCN give 36% conversion of pentenenitrile.				
CC	10 (Organic Chemistry)				
IT	4635-87-4P, 3-Pentenitrile				
	RL: PREP (Preparation)				
	(preparation of)				
IT	74-90-8, Hydrocyanic acid				
	(reaction with diolefins)				
IT	106-99-0, 1,3-Butadiene				
	(reactions of, with HCN)				
IT	4635-87-4E, 3-Pentenitrile				
	RL: PREP (Preparation)				
	(preparation of)				
RN	4635-87-4 CAPLUS				
CN	3-Pentenitrile (CA INDEX NAME)				



IT 74-90-8, Hydrocyanic acid  
 (reaction with diolefins)  
 RN 74-90-8 CAPLUS  
 CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, 1,3-Butadiene  
 (reactions of, with HCN)  
 RN 106-99-0 CAPLUS  
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 35 OF 60 CASREACT COPYRIGHT 2008 ACS ON STN  
 ACCESSION NUMBER: 138:304408 CASREACT Full-text  
 TITLE: Use of chelating phosphonites with transition metals  
 as catalysts  
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Kunsmann-keitel,  
 Dagmar Pasca; Haderlein, Gerd; Jungkamp, Tim;  
 Altmayer, Marco; Siegel, Wolfgang; Molnar, Ferenc  
 PATENT ASSIGNEE(S): BASF AG, Germany  
 SOURCE: Ger. Offen., 14 pp.  
 CODEN: GWXXBX  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 10150286	A1	20030417	DE 2001-10150286	20011012
CA 2462720	A1	20030424	CA 2002-2462720	20021004
WO 2003033142	A1	20030424	WO 2002-EP11108	20021004
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
AU 2002362816	A1	20030428	AU 2002-362816	20021004
EP 1438133	A1	20040721	EP 2002-801309	20021004
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK			
BR 2002013108	A	20040921	BR 2002-13108	20021004
CN 1568225	A	20050119	CN 2002-820102	20021004
JP 2005505611	T	20050224	JP 2003-535929	20021004

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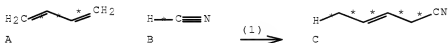
MX 2004PA02764	A	20040629	MX 2004-PA2764	20040324
US 2005090677	A1	20050428	US 2004-491911	20040408
IN 2004CN01013	A	20060203	IN 2004-CN1013	20040511
PRIORITY APPLN. INFO.:			DE 2001-10150286	20011012
			WO 2002-EP11108	20021004

OTHER SOURCE(S):                    MARPAT 138:304408  
GI

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB    Phosphonites I, II, and III (R1, R2, R4 = independently H, alkyl, C1-8 alkenyl, C1-8 alkoxy, R3 = H, Me, X = F, Cl, CF3, n = 0-2) are useful as ligands for nickel(0) catalyzed reactions. Thus, nickel(0)-(m-/p-tolylphosphite) catalyzed isomerization of 2-methyl-3-butenenitrile at 115° in 180 min gave 3-pentenitrile which in presence of same catalyst, ZnCl2 additive and HCN gave hydrocyanation product, adipodinitrile.

RX(1) OF 5        A + B ==> C...



RX(1)        RCT    A 106-99-0, B 74-90-8  
              PRO    C 4635-87-4  
              CAT    1295-35-8 Ni dicyclooctadiene, 179259-60-0 Phosphinous acid, diphenyl-, [1,1'-biphenyl]-2,2'-diyl ester  
              SOL    7732-18-5 Water, 109-99-9 THF  
              CON    180 minutes, 25 - 80 deg C

L88 ANSWER 36 OF 60    CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER:    138:304407    CASREACT    Full-text  
 TITLE:                    Use of chelating phosphonites with transition metals as catalysts  
 INVENTOR(S):            Bartsch, Michael; Baumann, Robert; Kunsmann-keitel, Dagmar Pasca; Haderlein, Gerd; Jungkamp, Tim; Altmayer, Marco; Siegel, Wolfgang; Molnar, Ferenc  
 PATENT ASSIGNEE(S):    BASF AG, Germany  
 SOURCE:                  Ger. Offen., 14 pp.  
                              CODEN: GWXXBX  
 DOCUMENT TYPE:        Patent  
 LANGUAGE:               German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

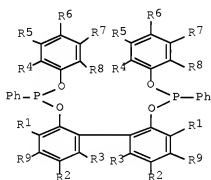
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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DE 10150285	A1	20030417	DE 2001-10150285	20011012
CA 2462719	A1	20030424	CA 2002-2462719	20021001

WO 2003033141 A1 20030424 WO 2002-EP10985 20021001  
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW  
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG  
AU 2002362813 A1 20030428 AU 2002-362813 20021001  
EP 1438132 A1 20040721 EP 2002-801302 20021001  
EP 1438132 B1 20070425  
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK  
BR 2002012966 A 20041013 BR 2002-12966 20021001  
CN 1568226 A 20050119 CN 2002-820103 20021001  
JP 2005505610 T 20050224 JP 2003-535928 20021001  
AT 360481 T 20070515 AT 2002-801302 20021001  
ES 2284977 T3 20071116 ES 2002-2801302 20021001  
MX 2004PA02437 A 20040629 MX 2004-PA2437 20040315  
US 2004235648 A1 20041125 US 2004-491964 20040408  
US 7022866 B2 20060404  
IN 2004CN01014 A 20060203 IN 2004-CN1014 20040511  
DE 2001-10150285 20011012  
WO 2002-EP10985 20021001

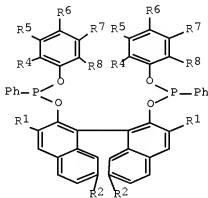
PRIORITY APPLN. INFO.:

OTHER SOURCE(S): MARPAT 138:304407

GI



I



II

AB Phosphonites I and II (R1, R2 = independently H, alkyl, C1-8 alkenyl, C1-8 alkoxy, R3 = H, Me, R4 = tert-Bu, R5, R6, R7, R8, R9 = H, alkyl, C1-8 alkenyl) are useful as ligands for nickel(0) catalyzed reactions. Thus, nickel(0)-(m-/p-tolylphosphite) catalyzed isomerization of 2-methyl-3-butenitrile at 115° in 180 min gave 3-pentenitrile which in presence of same catalyst, ZnCl2 additive and HCN gave hydrocyanation product, adipodinitrile.

RX(3) OF 5 H + E ==&gt; B...



RX(3) RCT H 106-99-0, E 74-90-8  
 PRO B 4635-87-4  
 CAT 125280-25-3 Nickel, tetrakis[tris(3(or 4)-methylphenyl]phosphite-kP]-  
 SOL 7732-18-5 Water, 109-99-9 THF  
 CON 180 minutes, 25 - 80 deg C

L88 ANSWER 37 OF 60 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 125:195996 CASREACT [Full-text](#)

TITLE: Hydrocyanation of diolefins and isomerization of nonconjugated 2-alkyl-3-monoalkenenitriles in liquid phase in presence of zero-valent nickel and multidentate phosphite ligands and preparation of phosphorochloridites and diaryl N,N-dialkylphosphoramidites

INVENTOR(S): Foo, Thomas; Garner, James Michael; Shapiro, Rafael; Tam, Wilson

PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA

SOURCE: PCT Int. Appl., 90 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 2

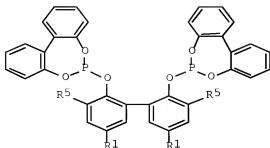
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9622968	A1	19960801	WO 1996-US548	19960117
W: BR, CA, CN, JP, KR, SG				
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
US 5821378	A	19981013	US 1995-563718	19951128
EP 804412	A1	19971105	EP 1996-902689	19960117
EP 804412	B1	19991201		
R: AT, BE, CH, DE, ES, FR, GB, IT, LI, NL, SE				
BR 9606718	A	19980113	BR 1996-6718	19960117
JP 10512879	T	19981208	JP 1996-522902	19960117
JP 3959111	B2	20070815		

PRIORITY APPLN. INFO.: US 1995-379429 19950127  
 US 1995-563718 19951128  
 WO 1996-US548 19960117

OTHER SOURCE(S): MARPAT 125:195996

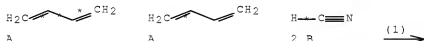
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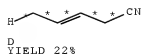
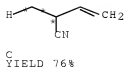


I

AB Improved liquid phase process useful in the hydrocyanation of diolefinic compds. to produce nonconjugated acyclic nitriles and in the liquid phase isomerization of the nitriles to 3- and/or 4-monoalkene linear nitriles. The improvement involves conducting the process in the presence of zero-valent Ni and a multidentate phosphite ligand. As an example of hydrocyanation, 0.201 g 25 weight% 1,3-butadiene in butyronitrile, 0.080 g 25 weight% HCN in propionitrile and 0.077 g of catalyst solution (0.014 g Ni(COD)<sub>2</sub>, 0.118 g I (R<sub>1</sub> = OMe, R<sub>5</sub> = tBu), 9.87 g propionitrile) were mixed and heated at 80°; after 1 h, 19.1% 3-pentenitrile and 75.5% 2-methyl-3-butenitrile were obtained; by comparison, use of Ni(P(OC<sub>6</sub>H<sub>4</sub>Me-p)<sub>3</sub>)<sub>4</sub>/P(OC<sub>6</sub>H<sub>4</sub>Me-p)<sub>3</sub> as catalyst gave 2.8 and 1.7%, resp. under similar conditions. As an example of isomerization, 93% of 2-methyl-3-butenitrile isomerized to 3-pentenitrile after 3 h in the presence of the Ni(COD)<sub>2</sub>/I (R<sub>1</sub> = OMe, R<sub>5</sub> = tBu) catalyst, whereas 25% conversion occurred in the presence of Ni(P(OC<sub>6</sub>H<sub>4</sub>Me-p)<sub>3</sub>)<sub>4</sub>/P(OC<sub>6</sub>H<sub>4</sub>Me-p)<sub>3</sub>. The invention also provides a novel method of making phosphorochloridites and diaryl N,N-dialkylphosphoramidites. As an example of synthesis of a diaryl N,N-dialkylphosphoramidite, to 25.0 g PCl<sub>3</sub> in 350 mL toluene was added 19.1 g dry iPr<sub>2</sub>NH at 5-7°, after which 19.4 g Et<sub>3</sub>N was added at 5-8°; after 16 h of stirring, a solution of 52.4 g thymol in 38.2 g Et<sub>3</sub>N and 50 mL dry toluene was added <40°, followed by 0.25 g 4-dimethylaminopyridine in 40 mL toluene; after workup, iPr<sub>2</sub>NP(OC<sub>6</sub>H<sub>3</sub>iPr-2-Me-5)<sub>2</sub> of 90-95% purity was obtained. As an example of synthesis of a phosphorochloridite, anhydrous HCl gas was bubbled into a solution of 7.21 g iPr<sub>2</sub>NP(OC<sub>6</sub>H<sub>4</sub>iPr-2)<sub>2</sub> in 200 mL cyclohexane at 0° over 20 min to give ClP(OC<sub>6</sub>H<sub>4</sub>iPr-2)<sub>2</sub>.

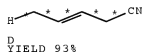
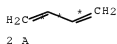
RX(1) OF 6      2 A + 2 B ==> C + D...





RX(1) RCT A 106-99-0, B 74-90-8  
 PRO C 16529-56-9, D 4635-87-4  
 CAT 1295-35-8 Ni dicyclooctadiene, 121627-17-6  
 Dibenzo[d,f][1,3,2]dioxaphosphopin, 6,6'-[[3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-  
 SOL 109-74-0 Butanenitrile, 107-12-0 Propionitrile

RX(6) OF 6 COMPOSED OF RX(1), RX(5)  
 RX(6) 2 A + 2 B ==> D



RX(1) RCT A 106-99-0, B 74-90-8  
 PRO C 16529-56-9, D 4635-87-4  
 CAT 1295-35-8 Ni dicyclooctadiene, 121627-17-6  
 Dibenzo[d,f][1,3,2]dioxaphosphopin, 6,6'-[[3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-  
 SOL 109-74-0 Butanenitrile, 107-12-0 Propionitrile

RX(5) RCT C 16529-56-9  
 PRO D 4635-87-4  
 CAT 1295-35-8 Ni dicyclooctadiene, 121627-17-6  
 Dibenzo[d,f][1,3,2]dioxaphosphopin, 6,6'-[[3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-  
 SOL 107-12-0 Propionitrile

L88 ANSWER 38 OF 60 USPATFULL ON STN  
 ACCESSION . . .  
 THIS PATENT.

AB A process is described for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, wherein the 1,3-butadiene and/or hydrogen cyanide is contacted with at least one microporous solid before the reaction. CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A process is described for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, wherein the 1,3-

- butadiene and/or hydrogen cyanide is contacted with at least one microporous solid before the reaction.
- SUMM The present invention relates to a process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst.
- SUMM . . . hydrocyanated to 3-pentenitrile. In a second, subsequent hydrocyanation, 3-pentenitrile is reacted with hydrogen cyanide to give adiponitrile. Both hydrocyanations are catalyzed by nickel(0)-phosphorus complexes.
- SUMM U.S. Pat. No. 3,852,329 describes a process for isomerizing 2-methyl-3-butenitrile over a nickel(0)-phosphorus complex as a catalyst to give 3-pentenitrile. In this isomerization, 2-methyl-3-butenitrile and/or the catalyst is contacted with a molecular sieve before the actual isomerization. According to U.S. Pat. No. 3,852,329 it is also possible to carry out the isomerization directly in the presence of a molecular sieve.
- SUMM U.S. Pat. No. 3,846,474 describes a process for hydrocyanating 3-pentenitrile over a nickel(0)-phosphorus catalyst. In this process, 3-pentenitrile is contacted with a molecular sieve before the hydrocyanation. Alternatively, it is possible that the molecular sieve is used during the hydrocyanation or the catalyst solution is treated with a molecular sieve before it is used in the hydrocyanation.
- SUMM . . . the present invention to provide a process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the catalyst used in the process having a high lifetime.
- SUMM . . . of this object starts from a process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst. In a first embodiment, the process according to the invention comprises contacting 1,3-butadiene and/or hydrogen cyanide with at least one microporous solid before the reaction.
- SUMM It has been found in accordance with the invention that the contacting of 1,3-butadiene with the at least one microporous solid increases the lifetime of the nickel(0)-phosphorus catalyst. Without being bound to a theory, the effect of the increased lifetime of the catalyst is attributed to the removal of water and of the tert-butylpyrocatechol stabilizer.
- SUMM . . . to the invention, the 1,3-butadiene and the hydrogen cyanide may be contacted together or separately with the at least one microporous solid. It is preferred that the 1,3-butadiene and/or the hydrogen cyanide are freed of the at least one microporous solid before the actual hydrocyanation with the at least one catalyst.
- SUMM . . . the present invention relates to a process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide with at least one catalyst, the process according to the invention comprising effecting the hydrocyanation in the presence of the at least one microporous solid.
- SUMM When the hydrocyanation is carried out in semibatchwise operation, it is preferred that the reactor is initially charged with the catalyst components and 1,3-butadiene, while hydrogen cyanide is metered into the reaction mixture over the reaction time.
- SUMM . . . a solvent is used, the solvent should be liquid and inert toward the unsaturated compounds and the at least one catalyst at the given reaction temperature and the given reaction pressure. In general, the solvents used are hydrocarbons, for example benzene. . .
- SUMM . . . charging the apparatus with all reactants. However, it is preferred when the apparatus is filled with the at least one catalyst, 1,3-butadiene and, if appropriate, the solvent. The gaseous hydrogen cyanide preferably floats over the surface of the reaction mixture or.



. . . reaction mixture. A further procedure for charging the apparatus is the filling of the apparatus with the at least one catalyst, hydrogen cyanide and, if appropriate, the solvent, and slowly feeding the 1,3-butadiene to the reaction mixture. Alternatively, it is also. .

SUMM . . . the pressure in the reactor is such that all reactants such as 1,3-butadiene, hydrogen cyanide and the at least one catalyst are metered in in liquid form and are present in the liquid phase in the reaction mixture. A solid suspended. . . phase may be present in the reaction mixture and may also be metered in together with the at least one catalyst, for example consisting of degradation products of the catalyst system, comprising nickel(II) compounds inter alia.

SUMM The macroporous solid obtained after the treatment of the 1,3-butadiene and/or hydrogen cyanide, or the microporous solid used in the hydrocyanation, may, after it has been used, be regenerated by heating under reduced pressure in an atmosphere which is formed by gases selected from the group consisting of noble gases, air and oxygen. It is thus possible to use the microporous solid again.

SUMM The at least one microporous solid used in the process according to the invention is preferably selected from the group consisting of aluminas and molecular sieves, and preferably has a particle size of from 0.01 to 20 mm, more preferably from 0.1 to 10 mm, in. . .

SUMM When alumina is used as the microporous solid in the process according to the invention, the alumina may be contaminated with rare earth metal compounds, alkali metal. . .

SUMM When the microporous solid used in the process according to the invention is a molecular sieve, this refers to molecular sieves having an average pore radius of from 0.1 to 20 Å, preferably from 1 to 10 Å.

SUMM When the 1,3-butadiene, before the actual hydrocyanation over the at least one nickel(0)-phosphorus catalyst, is contacted with the at least one microporous solid, it is advantageous subsequently to store and transport it, before the actual hydrocyanation of the 1,3-butadiene, at temperatures of. . .

SUMM The inventive treatment of the feed streams for the above-described hydrocyanation with molecular sieve or alumina result in residual water contents in the reaction mixture of less than 1000 ppm, more preferably less than. . .

DETD This example illustrates the need to dry butadiene before it is contacted with a catalyst system, suitable for the hydrocyanation, of Ni(0) complex with, for example, tritolyl phosphite as a ligand.

DETD . . . from brine cooling to heating with throttle-controlled 35 bar steam. The bed was then flowed through with 1 m.sup.3/h of nitrogen and heated gradually to 210° C. over three days. When the end temperature had been attained, the steam heating was switched off and the bed was flowed through with nitrogen until 60° C. had been attained in the interior of the bed. Reconnecting the jacket again to brine cooling cooled. . .

DETD On the Drying with Molecular Sieve

DETD A vessel made of boilerplate (diameter 50 mm) was charged with a 200 mm-high bed of molecular sieve from Karl Roth GmbH (product number 4062020) and cooled to 0° C. using a jacket. Subsequently, butadiene was introduced at. . .

DETD 2.24 mol of butadiene dried over a bed of 4 Å molecular sieve, 1.62 mol of HCN and 14 mmol of Ni in the form of nickel(0)(m-/p-tolyl phosphite) were fed per hour into. . .

CLM What is claimed is:

1. A process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the

process comprising contacting 1,3-butadiene with at least one microporous solid, and releasing the 1,3-butadiene from the at least one microporous solid before the hydrocyanation; and regenerating the at least one microporous solid which had been contacted with 1,3-butadiene or hydrogen cyanide by heating under reduced pressure in an atmosphere comprising one or more gases selected from the group consisting of noble gases, air and nitrogen.

. . . to claim 1, further comprising contacting hydrogen cyanide together with or separately from the 1,3-butadiene with the at least one microporous solid.

3. The process according to claim 1, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of 1,3-butadiene are selected in such a way to provide plug flow characteristics over the at least one microporous solid.

4. A process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, in the presence of at least one microporous solid.

5. The process according to claim 4, further comprising regenerating the at least one microporous solid by heating under reduced pressure in an atmosphere comprising one or more gases from the group consisting of noble gases, air and nitrogen.

7. The process according to claim 1, wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 nm.

8. The process according to claim 1, wherein the microporous solid has a porosity which is between 0 and 80% based on the particle volume.

9. The process according to claim 1, wherein the microporous solid is in extrudate form, in round form or in undefined form as a result of fracturing.

10. The process according to claim 2, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of the hydrogen cyanide are selected in such a way to . . .

12. The process according to claim 4, wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 nm.

13. A process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the process comprising: contacting at least one microporous solid with the 1,3-butadiene and hydrogen cyanide; directing the the 1,3-butadiene and the hydrogen cyanide that had contacted the at least one microporous solid to a hydrocyanation reaction system; and regenerating the at least one microporous solid that had been contacted with the 1,3-butadiene and hydrogen cyanide by heating under reduced pressure in an atmosphere comprising one or more gases selected from the group consisting of noble gases, air and nitrogen.

14. The process according to claim 13, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of 1,3-butadiene and hydrogen cyanide are selected to provide plug flow characteristics over the at least one microporous solid.

16. The process according to claim 13 wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 nm.

17. The process according to claim 16 wherein the microporous solid has a porosity which is between 0 and 80% based on the particle volume.

IT Air

(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile using)

IT 4635-67-4P, 3-Pentenitrile

(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,

1,3-Butadiene, reactions

(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)

PI US 2007155977

A1 20070705

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AB A process is described for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, wherein the 1,3-butadiene and/or hydrogen cyanide is contacted with at least one microporous solid before the reaction.

SUMM The present invention relates to a process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst.

SUMM Adiponitrile is an important starting material in nylon production and is obtained by double hydrocyanation of 1,3-butadiene. In a first hydrocyanation, 1,3-butadiene is hydrocyanated to 3-pentenitrile. In a second, subsequent hydrocyanation, 3-pentenitrile is reacted with hydrogen cyanide to give adiponitrile. Both hydrocyanations are catalyzed by nickel(0)-phosphorus complexes.

SUMM U.S. Pat. No. 3,852,329 describes a process for isomerizing 2-methyl-3-butenitrile over a nickel(0)-phosphorus complex as a catalyst to give 3-pentenitrile. In this isomerization, 2-methyl-3-butenitrile and/or the catalyst is contacted with a molecular sieve before the actual isomerization. According to U.S. Pat. No. 3,852,329 it is also possible to carry out the isomerization directly in the presence of a molecular sieve.

SUMM U.S. Pat. No. 3,846,474 describes a process for hydrocyanating 3-pentenitrile over a nickel(0)-phosphorus catalyst. In this process, 3-pentenitrile is contacted with a molecular sieve before the hydrocyanation. Alternatively, it is possible that the molecular sieve is used during the hydrocyanation or the catalyst solution is treated with a molecular sieve before it is used in the hydrocyanation.

SUMM It is thus an object of the present invention to provide a process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the catalyst used in the process having a high lifetime.

SUMM The inventive achievement of this object starts from a process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst. In a first embodiment, the process according to the invention comprises contacting 1,3-butadiene and/or

hydrogen cyanide with at least one microporous solid before the reaction.

SUMM It has been found in accordance with the invention that the contacting of 1,3-butadiene with the at least one microporous solid increases the lifetime of the nickel(0)-phosphorus catalyst. Without being bound to a theory, the effect of the increased lifetime of the catalyst is attributed to the removal of water and of the tert-butylpyrocatechol stabilizer.

SUMM In the process according to the invention, the 1,3-butadiene and the hydrogen cyanide may be contacted together or separately with the at least one microporous solid. It is preferred that the 1,3-butadiene and/or the hydrogen cyanide are freed of the at least one microporous solid before the actual hydrocyanation with the at least one catalyst.

SUMM In a second embodiment, the present invention relates to a process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide with at least one catalyst, the process according to the invention comprising effecting the hydrocyanation in the presence of the at least one microporous solid.

SUMM When the hydrocyanation is carried out in semibatchwise operation, it is preferred that the reactor is initially charged with the catalyst components and 1,3-butadiene, while hydrogen cyanide is metered into the reaction mixture over the reaction time.

SUMM The hydrocyanation may be carried out in the presence or in the absence of a solvent. When a solvent is used, the solvent should be liquid and inert toward the unsaturated compounds and the at least one catalyst at the given reaction temperature and the given reaction pressure. In general, the solvents used are hydrocarbons, for example benzene or xylene, or nitrites, for example acetonitrile or benzonitrile. However, preference is given to using a ligand as the solvent.

SUMM The hydrocyanation reaction may be carried out by charging the apparatus with all reactants. However, it is preferred when the apparatus is filled with the at least one catalyst, 1,3-butadiene and, if appropriate, the solvent. The gaseous hydrogen cyanide preferably floats over the surface of the reaction mixture or is preferably passed through the reaction mixture. A further procedure for charging the apparatus is the filling of the apparatus with the at least one catalyst, hydrogen cyanide and, if appropriate, the solvent, and slowly feeding the 1,3-butadiene to the reaction mixture. Alternatively, it is also possible that the reactants are introduced into the reactor and the reaction mixture is brought to the reaction temperature at which the hydrogen cyanide is added to the mixture in liquid form. In addition, the hydrogen cyanide may also be added before heating to reaction temperature. The reaction is carried out under conventional hydrocyanation conditions for temperature, atmosphere, reaction time, etc.

SUMM In a further embodiment, the hydrocyanation may be carried out in the liquid phase, in which case the pressure in the reactor is such that all reactants such as 1,3-butadiene, hydrogen cyanide and the at least one catalyst are metered in in liquid form and are present in the liquid phase in the reaction mixture. A solid suspended phase may be present in the reaction mixture and may also be metered in together with the at least one catalyst, for example consisting of degradation products of the catalyst system, comprising nickel(II) compounds inter alia.

- SUMM The microporous solid obtained after the treatment of the 1,3-butadiene and/or hydrogen cyanide, or the microporous solid used in the hydrocyanation, may, after it has been used, be regenerated by heating under reduced pressure in an atmosphere which is formed by gases selected from the group consisting of noble gases, air and oxygen. It is thus possible to use the microporous solid again.
- SUMM The at least one microporous solid used in the process according to the invention is preferably selected from the group consisting of aluminas and molecular sieves, and preferably has a particle size of from 0.01 to 20 mm, more preferably from 0.1 to 10 mm, in particular from 1 to 5 mm. The porosity of the shaped bodies is between 0 and 80% based on the particle volume. It is possible to use particles either in the form of extrudates or in round form, or in undefined form as a result of fracturing.
- SUMM When alumina is used as the microporous solid in the process according to the invention, the alumina may be contaminated with rare earth metal compounds, alkali metal compounds or alkaline earth metal compounds in the range from 0 to 20% by weight, more preferably from 0 to 10% by weight, based in each case on the solid mass used.
- SUMM When the microporous solid used in the process according to the invention is a molecular sieve, this refers to molecular sieve having an average pore radius of from 0.1 to 20 Å, preferably from 1 to 10 Å.
- SUMM When the 1,3-butadiene, before the actual hydrocyanation over the at least one nickel(0)-phosphorus catalyst, is contacted with the at least one microporous solid, it is advantageous subsequently to store and transport it, before the actual hydrocyanation of the 1,3-butadiene, at temperatures of less than 50° C., more preferably less than 20° C., in particular less than 0° C., in order to prevent polymerizations.
- SUMM The inventive treatment of the feed streams for the above-described hydrocyanation with molecular sieve or alumina result in residual water contents in the reaction mixture of less than 1000 ppm, more preferably less than 100 ppm, in particular less than 10 ppm, of water.
- DETD This example illustrates the need to dry butadiene before it is contacted with a catalyst system, suitable for the hydrocyanation, of Ni(0) complex with, for example, tritolyl phosphite as a ligand.
- DETD The apparatus described in Example 1 with the bed detailed there was charged with butadiene until the water content in the outlet stream had risen to a measured value of 50 ppm by weight of water. The butadiene feed was then stopped. Subsequently, the jacket was switched from brine cooling to heating with throttle-controlled 35 bar steam. The bed was then flowed through with 1 m.sup.3/h of nitrogen and heated gradually to 210° C. over three days. When the end temperature had been attained, the steam heating was switched off and the bed was flowed through with nitrogen until 60° C. had been attained in the interior of the bed. Reconnecting the jacket again to brine cooling cooled the bed back to 0° C. and butadiene was then introduced again. After the wetting had been completed, the water meter at the outlet was brought back into operation. The measurements were again at 1 ppm by weight of water based on butadiene.
- DETD On the Drying with Molecular Sieve

DETD A vessel made of boilerplate (diameter 50 mm) was charged with a 200 mm-high bed of molecular sieve from Karl Roth GmbH (product number 4062020) and cooled to 0° C. using a jacket. Subsequently, butadiene was introduced at a mass flow rate of 100 g/h. At the outlet of the bed, a measuring instrument for determining water in butadiene (from General Eastern, AMY 170) did not find any detectable amounts of water over a period of two weeks. Accordingly, the butadiene was dry after it had flowed through the bed.

DETD 2.24 mol of butadiene dried over a bed of 4 Å molecular sieve, 1.62 mol of HCN and 14 mmol of Ni in the form of nickel(0) (m-/p-tolyl phosphite) were fed per hour into a stirred pressure reactor (pressure: 15 bar, internal temperature 105° C., residence time: approx. 40 min/reactor). According to quantitative analysis, the HCN conversion is quantitative (Vollhard titration). The 2M3BN/3PN ratio of the reaction effluent is determined by GC chromatography (GC area percent). The 2M3BN/3PN ratio was 1.82/1. The loss of Ni(0) based on product of value formed was 0.33 kg of Ni(0)/t of product of value (3PN/2M3BN).

1. A process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the process comprising contacting 1,3-butadiene with at least one microporous solid, and releasing the 1,3-butadiene from the at least one microporous solid before the hydrocyanation; and regenerating the at least one microporous solid which had been contacted with 1,3-butadiene or hydrogen cyanide by heating under reduced pressure in an atmosphere comprising one or more gases selected from the group consisting of noble gases, air and nitrogen.

2. The process according to claim 1, further comprising contacting hydrogen cyanide together with or separately from the 1,3-butadiene with the at least one microporous solid.

3. The process according to claim 1, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of 1,3-butadiene are selected in such a way to provide plug flow characteristics over the at least one microporous solid.

4. A process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, in the presence of at least one microporous solid.

5. The process according to claim 4, further comprising regenerating the at least one microporous solid by heating under reduced pressure in an atmosphere comprising one or more gases from the group consisting of noble gases, air and nitrogen.

7. The process according to claim 1, wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 nm.

8. The process according to claim 1, wherein the microporous solid has a porosity which is between 0 and 80% based on the particle volume.

9. The process according to claim 1, wherein the microporous solid is in extrudate form, in round form or in undefined form as a result of fracturing.

10. The process according to claim 2, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of the hydrogen cyanide are selected in such a way to provide flow characteristics.

12. The process according to claim 4, wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 mm.

13. A process for preparing 3-pentenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the process comprising: contacting at least one microporous solid with the 1,3-butadiene and hydrogen cyanide; directing the the 1,3-butadiene and the hydrogen cyanide that had contacted the at least one microporous solid to a hydrocyanation reaction system; and regenerating the at least one microporous solid that had been contacted with the 1,3-butadiene and hydrogen cyanide by heating under reduced pressure in an atmosphere comprising one or more gases selected from the group consisting of noble gases, air and nitrogen.

14. The process according to claim 13, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of 1,3-butadiene and hydrogen cyanide are selected to provide plug flow characteristics over the at least one microporous solid.

16. The process according to claim 13 wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 mm.

17. The process according to claim 16 wherein the microporous solid has a porosity which is between 0 and 80% based on the particle volume.

- IT Air  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile using)
- IT 4635-87-4P, 3-Pentenitrile  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-8,  
1,3-Butadiene, reactions  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- IT 4635-87-4P, 3-Pentenitrile  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- RN 4635-87-4 USPATFULL
- CN 3-Pentenitrile (CA INDEX NAME)



- IT 74-90-8, Hydrogen cyanide, reactions 106-99-8,  
1,3-Butadiene, reactions  
(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenitrile)
- RN 74-90-8 USPATFULL

10/586490

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 39 OF 60 USPATFULL on STN

ACCESSION NUMBER: 2007:128858 USPATFULL Full-text

TITLE: Method for the separation of pentenenitrile isomers

INVENTOR(S): Jungkamp, Tim, Kapellen, BELGIUM

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	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2007112215	A1	20070517	<--
APPLICATION INFO.:	US 2005-586452	A1	20050126	(10)
	WO 2005-EP726		20050126	
			20060718	PCT 371 date

	NUMBER	DATE
PRIORITY INFORMATION:	DE 2004-10200400472120040129	
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	CONNOLLY BOVE LODGE & HUTZ LLP, P.O. BOX 2207, WILMINGTON, DE, 19899-2207, US	
NUMBER OF CLAIMS:	14	
EXEMPLARY CLAIM:	1	
LINE COUNT:	1081	

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A process is described for separating mixtures of isomeric pentenenitriles, in which at least one isomer is removed from the mixture, wherein the separation of the substance mixtures of isomeric pentenenitriles is effected distillatively under reduced pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.



- SUMM . . . and 4-vinylcyclohexene. In a second hydrocyanation, 3-pentenitrile is subsequently reacted with hydrogen cyanide to give adiponitrile, likewise over a nickel catalyst, but with addition of a Lewis acid. In this second hydrocyanation too, a mixture of the reactant and product nitriles. . . .
- SUMM . . . Pat. No. 3,852,325 and U.S. Pat. No. 3,852,327 to convert the pentenenitrile isomers which are difficult to remove by distillation catalytically to those which can easily be removed by distillation.
- SUMM A disadvantage is that the catalytic isomerization leads to losses of products of value as a result of formation of undesired isomers or oligomers.
- SUMM . . . the resulting organic phase first has to be freed completely of water before further use in hydrocyanation reactions using nickel(0) catalysts with phosphorus(III) ligands, since the phosphorus(III) ligands are otherwise irreversibly hydrolyzed and thus deactivated. A further disadvantage in this process. . . .
- SUMM The hydrocyanation of butadiene to 3-pentenitrile and mixtures thereof with 2-methyl-3-butenitrile are carried out in the presence of a nickel(0) catalyst.
- SUMM The Ni(0) catalysts are complexes, which contain phosphorus ligands and/or free phosphorus ligands preferably homogeneously dissolved nickel(0) complexes.
- SUMM . . . to in the context of the present invention as 3-pentenitrile. However, the 2-methyl-3-butenitrile occurring in the hydrocyanation, depending on the catalyst system, in at least double-digit percentages, based on the sum of all pentenenitrile isomers formed, has to be removed before. . . .
- SUMM . . . comprise 2-methyl-3-butenitrile and 3-pentenitrile. These mixtures are preferably obtained in a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst, the hydrocyanation effluent typically comprising a proportion of 1,3-butadiene unconverted in the hydrocyanation which can be removed at least partly by suitable processes, and the catalyst content present in the product stream obtained in this way being removable by suitable processes. Processes of this type are. . . 004 720 and DE-A-102 004 004 724. However, it is not necessarily obligatory to remove the unconverted 1,3-butadiene and the catalyst content.
- SUMM The nickel(0)-containing catalyst systems can be prepared by processes known per se.
- SUMM The ligands used for the isomerization catalyst may be the same phosphorus ligands as for the above-described hydrocyanation.
- SUMM . . . 4,874,884, it is possible to use synergistically active combinations of Lewis acids, in order to increase the activity of the catalyst system. Suitable promoters may, for example, be selected from the group consisting of CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3 and (C.sub.6H.sub.5).sub.3SnX where. . . .
- SUMM . . . advantageous when the isomerization is carried out in a nonoxidative atmosphere, for example under a protective gas atmosphere composed of nitrogen or a noble gas such as argon.
- SUMM The cis-2-pentenitrile removed may be isomerized thermally or under catalysis to the 3-pentenitrile product of value. Mixtures having substantially trans-2-pentenitrile, trans-3-pentenitrile and unconverted cis-2-pentenitrile are obtained. A prerequisite for the. . . .
- SUMM . . . comprises cis-2-pentenitrile and 3-pentenitrile. These mixtures stem, for example, from a reaction of 3-pentenitrile with hydrogen cyanide over a hydrocyanation catalyst. In addition, these mixtures may stem from the thermal or catalyzed isomerization of cis-2-pentenitrile.
- SUMM . . . hydrocyanation reaction. Secondly, it is also possible to add

to this circulation stream pentenenitriles which remain after the removal of catalyst constituents in the adiponitrile-containing product stream and are removed from this stream for the purpose of recycling, as described in. . .

SUMM . . . invention is accordingly intended preferentially for mixtures which stem from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst, or from an isomerization of 2-methyl-3-butenitrile or from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.

CLM What is claimed is:

- . . . the mixture comprises 2-methyl-3-butenitrile and 3-pentenenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst.
- . . . mixture comprises cis-2-pentenenitrile and 3-pentenenitrile and stems is produced from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.
- . . . the mixture comprises (E)-2-methyl-2-butenitrile and 3-pentenenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst or from the isomerization of 2-methyl-3-butenitrile or from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.
- . . . the mixture comprises 2-methyl-3-butenitrile and 3-pentenenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst.
- . . . the mixture comprises cis-2-pentenenitrile and 3-pentenenitrile and is produced from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.
- . . . mixture comprises (E)-2-methyl-2-butenitrile and 3-pentenenitrile and is produced from a reaction of 1, 3-butadiene with hydrogen cyanide over a hydrocyanation catalyst or from the isomerization of 2-methyl-3-butenitrile or from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.

IT 4635-97-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P, cis-2-Methyl-2-butenitrile 25899-50-7P, cis-2-Pentenenitrile 27236-41-5P, Pentenenitrile 30574-97-1P, trans-2-Methyl-2-butenitrile (vacuum distillation method for the separation of pentenenitrile isomers)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions (vacuum distillation method for the separation of pentenenitrile isomers prepared from)

PI US 2007112215 A1 20070517 <--|

SUMM Adiponitrile, an important intermediate in nylon production, is prepared by double hydrocyanation of 1,3-butadiene. In a first hydrocyanation stage, 1,3-butadiene is reacted with hydrogen cyanide in the presence of nickel(0) which is stabilized with phosphorus ligands to give 3-pentenenitrile. Secondary components of this first hydrocyanation are substantially 2-methyl-3-butenitrile, 2-pentenenitriles, 2-methyl-2-butenitriles, C.sub.9 nitriles, methylglutaronitrile and 4-vinylcyclohexene. In a second hydrocyanation, 3-pentenenitrile is subsequently reacted with hydrogen cyanide to give adiponitrile, likewise over a nickel catalyst, but with addition of a Lewis acid. In

this second hydrocyanation too, a mixture of the reactant and product nitriles and also the abovementioned secondary components is obtained.

- SUMM To circumvent a separation of trans-3-pentenitrile and trans-2-pentenitrile, it is proposed, for example in U.S. Pat. No. 3,526,654, U.S. Pat. No. 3,564,040, U.S. Pat. No. 3,852,325 and U.S. Pat. No. 3,852,327 to convert the pentenenitrile isomers which are difficult to remove by distillation catalytically to those which can easily be removed by distillation.
- SUMM A disadvantage is that the catalytic isomerization leads to losses of products of value as a result of formation of undesired isomers or oligomers.
- SUMM To circumvent a separation of (Z)-2-methyl-2-butenitrile and 2-methyl-3-butenitrile, and also trans-2-pentenitrile and trans-3-pentenitrile, U.S. Pat. No. 3,865,865 proposes treating the nitrile mixture with aqueous sulfite solution, in each case to obtain an aqueous phase comprising the particular bisulfite adducts of the conjugated nitrites (Z)-2-methyl-2-butenitrile or trans-2-pentenitrile, and an organic phase depleted in these nitrites. A disadvantage in this process is that the resulting organic phase first has to be freed completely of water before further use in hydrocyanation reactions using nickel(0) catalysts with phosphorus(III) ligands, since the phosphorus(III) ligands are otherwise irreversibly hydrolyzed and thus deactivated. A further disadvantage in this process is that the resulting bisulfite adducts can only be dissociated for the purpose of further using the conjugated nitriles, as described in U.S. Pat. No. 3,865,865, only under drastic conditions and only with moderate yield.
- SUMM The hydrocyanation of butadiene to 3-pentenitrile and mixtures thereof with 2-methyl-3-butenitrile are carried out in the presence of a nickel(0) catalyst.
- SUMM The Ni(0) catalysts are complexes, which contain phosphorus ligands and/or free phosphorus ligands preferably homogeneously dissolved nickel(0) complexes.
- SUMM The desired products of this hydrocyanation which can be used for preparing adiponitrile are trans-3-pentenitrile, cis-3-pentenitrile and 4-pentenitrile, which are referred to in the context of the present invention as 3-pentenitrile. However, the 2-methyl-3-butenitrile occurring in the hydrocyanation, depending on the catalyst system, in at least double-digit percentages, based on the sum of all pentenenitrile isomers formed, has to be removed before the further processing of the hydrocyanation effluent. The specification for the depletion of 2-methyl-3-butenitrile in the 3-pentenitrile is strict and has to be complied with because methylglutaronitrile (MGN), an undesired by-product of adiponitrile production, would form from 2-methyl-3-butenitrile in the subsequent hydrocyanation. However, the complex apparatus and the energy requirements for the virtually complete removal of 2-methyl-3-butenitrile from 3-pentenitrile is very high and is determined by the relative volatility, defined as the ratio of the vapor pressures of these two substances, which is approx. 1.7 at atmospheric pressure, derived from the known standard boiling points of 416.8 K for trans-3-pentenitrile and 396.1 K for 2-methyl-3-butenitrile. It has been found in accordance with the invention that the relative volatility of 2-methyl-3-butenitrile and 3-pentenitrile increases at pressures below atmospheric pressure.

SUMM Accordingly, the process according to the invention is determined in one embodiment I for separating mixtures which comprise 2-methyl-3-butenenitrile and 3-pentenitrile. These mixtures are preferably obtained in a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst, the hydrocyanation effluent typically comprising a proportion of 1,3-butadiene unconverted in the hydrocyanation which can be removed at least partly by suitable processes, and the catalyst content present in the product stream obtained in this way being removable by suitable processes. Processes of this type are described, for example, in DE-A-102 004 004 720 and DE-A-102 004 004 724. However, it is not necessarily obligatory to remove the unconverted 1,3-butadiene and the catalyst content.

SUMM The nickel(0)-containing catalyst systems can be prepared by processes known per se.

SUMM The ligands used for the isomerization catalyst may be the same phosphorus ligands as for the above-described hydrocyanation.

SUMM Useful Lewis acids are inorganic or organic metal compounds in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include ZnBr.sub.2, ZnI.sub.2, ZnCl.sub.2, ZnSO.sub.4, CuCl.sub.2, CuCl, Cu(O.sub.3SCF.sub.3).sub.2, CoCl.sub.2, CoI.sub.2, FeI.sub.2, FeCl.sub.3, FeCl.sub.2, FeCl.sub.2(THF).sub.2, TiCl.sub.4(THF).sub.2, TiCl.sub.4, TiCl.sub.3, ClTi(O-i-propyl).sub.3, MnCl.sub.2, SnCl.sub.3, AlCl.sub.3, (C.sub.8H.sub.17)AlCl.sub.2, (C.sub.8H.sub.17).sub.2AlCl, (i-C.sub.4H.sub.9).sub.2AlCl, (C.sub.6H.sub.5).sub.2AlCl, (C.sub.6H.sub.5)AlCl.sub.2, ReCl.sub.5, ZrCl.sub.4, NbCl.sub.5, VCl.sub.3, CrCl.sub.2, MoCl.sub.5, YCl.sub.3, CdCl.sub.2, LaCl.sub.3, Er(O.sub.3SCF.sub.3).sub.3, Yb(O.sub.2CCF.sub.3).sub.3, SmCl.sub.3, B(C.sub.6H.sub.5).sub.3, TaCl.sub.5, as described, for example, in U.S. Pat. No. 6,127,567, U.S. Pat. No. 6,171,996 and U.S. Pat. No. 6,380,421. Also useful are metal salts such as ZnCl.sub.2, CoI.sub.2 and SnCl.sub.2, and organometallic compounds such as RAlCl.sub.2, R.sub.2AlCl, RSnO.sub.3SCF.sub.3 and R.sub.3B, where R is an alkyl or aryl group, as described, for example, in U.S. Pat. No. 3,496,217, U.S. Pat. No. 3,496,218 and U.S. Pat. No. 4,774,353. According to U.S. Pat. No. 3,773,809, the promoter used may also be a metal in cationic form which is selected from the group consisting of zinc, cadmium, beryllium, aluminum, gallium, indium, thallium, titanium, zirconium, hafnium, erbium, germanium, tin, vanadium, niobium, scandium, chromium, molybdenum, tungsten, manganese, rhenium, palladium, thorium, iron and cobalt, preferably zinc, cadmium, titanium, tin, chromium, iron and cobalt, and the anionic moiety of the compound may be selected from the group consisting of halides such as fluoride, chloride, bromide and iodide, anions of lower fatty acids having from 2 to 7 carbon atoms, HPO.sub.3.sub.2-, H.sub.3PO.sub.2-, CF.sub.3COO.sub.-, C.sub.7H.sub.15OSO.sub.2.sub.- or SO.sub.4.sub.2-. Further suitable promoters disclosed by U.S. Pat. No. 3,773,809 are borohydrides, organoborohydrides and boric esters of the formula R.sub.3B and B(OR).sub.3, where R is selected from the group consisting of hydrogen, aryl radicals having from 6 to 18 carbon atoms, aryl radicals substituted by alkyl groups having from 1 to 7 carbon atoms and aryl radicals substituted by cyano-substituted alkyl groups having from 1 to 7 carbon atoms, advantageously triphenylboron. Moreover, as described in U.S. Pat. No. 4,874,884, it is possible to use synergistically active combinations of Lewis acids, in order to increase the activity of the catalyst system. Suitable promoters may, for

example, be selected from the group consisting of CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3 and (C.sub.6H.sub.5).sub.3SnX where X.dbd.CF.sub.3SO.sub.3, CH.sub.3C.sub.6H.sub.4SO.sub.3 or (C.sub.6H.sub.5).sub.3BCN, and the preferred ratio specified of promoter to nickel is from about 1:16 to about 50:1.

SUMM In addition, it has been found to be advantageous when the isomerization is carried out in a nonoxidative atmosphere, for example under a protective gas atmosphere composed of nitrogen or a noble gas such as argon.

SUMM The cis-2-pentenitrile removed may be isomerized thermally or under catalysis to the 3-pentenitrile product of value. Mixtures having substantially trans-2-pentenitrile, trans-3-pentenitrile and unconverted cis-2-pentenitrile are obtained. A prerequisite for the insertion of this isomerization step into an integrated process for preparing adiponitrile is that the removal of cis-2-pentenitrile from this mixture is realizable economically.

SUMM According to embodiment 11, the present invention thus relates to a process for separating mixtures of isomeric pentenenitriles, wherein the separation is effected distillatively under reduced pressure and the mixture comprises cis-2-pentenitrile and 3-pentenitrile. These mixtures stem, for example, from a reaction of 3-pentenitrile with hydrogen cyanide over a hydrocyanation catalyst. In addition, these mixtures may stem from the thermal or catalyzed isomerization of cis-2-pentenitrile.

SUMM In the hydrocyanation process of 3-pentenitrile to adiponitrile, (E)-2-methyl-2-butenitrile accordingly accumulates in some cases in the 3-pentenitrile circulation stream. This circulation stream, as a mixture of pentenenitriles, may be composed, for example, firstly of the proportion of pentenenitriles which are removed directly after the hydrocyanation reaction. Secondly, it is also possible to add to this circulation stream pentenenitriles which remain after the removal of catalyst constituents in the adiponitrile-containing product stream and are removed from this stream for the purpose of recycling, as described in DE-A-102 004 004 683, filed at the same time as the present application.

SUMM According to embodiment IV, the process according to the invention is accordingly intended preferentially for mixtures which stem from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst, or from an isomerization of 2-methyl-3-butenitrile or from a reaction of 3-pentenitrile with hydrogen cyanide over a hydrocyanation catalyst.

3. The process according to claim 1, wherein the mixture comprises 2-methyl-3-butenitrile and 3-pentenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst.

7. The process according to claim 1, wherein the mixture comprises cis-2-pentenitrile and 3-pentenitrile and stems is produced from a reaction of 3-pentenitrile with hydrogen cyanide over a hydrocyanation catalyst.

9. The process according to claim 1, wherein the mixture comprises (E)-2-methyl-2-butenitrile and 3-pentenitrile and is produced from a

reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst or from the isomerization of 2-methyl-3-butenitrile or from a reaction of 3-pentenitrile with hydrogen cyanide over a hydrocyanation catalyst.

11. The process according to claim 2, wherein the mixture comprises 2-methyl-3-butenitrile and 3-pentenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst.

13. The process according to claim 2 wherein the mixture comprises cis-2-pentenitrile and 3-pentenitrile and is produced from a reaction of 3-pentenitrile with hydrogen cyanide over a hydrocyanation catalyst.

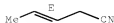
14. The process according to claim 2, wherein the mixture comprises (E)-2-methyl-2-butenitrile and 3-pentenitrile and is produced from a reaction of 1, 3-butadiene with hydrogen cyanide over a hydrocyanation catalyst or from the isomerization of 2-methyl-3-butenitrile or from a reaction of 3-pentenitrile with hydrogen cyanide over a hydrocyanation catalyst.

IT 4625-87-4P, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile 16529-66-1P, trans-3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile 20068-02-4P, cis-2-Methyl-2-butenitrile 25899-50-7P, cis-2-Pentenitrile 27236-41-5P, Pentenitrile 30574-97-1P, trans-2-Methyl-2-butenitrile (vacuum distillation method for the separation of pentenitrile isomers)  
IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions (vacuum distillation method for the separation of pentenitrile isomers prepared from)  
IT 4635-87-4P, 3-Pentenitrile 16529-66-1P, trans-3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile (vacuum distillation method for the separation of pentenitrile isomers)  
RN 4635-87-4 USPATFULL  
CN 3-Pentenitrile (CA INDEX NAME)



RN 16529-66-1 USPATFULL  
CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 USPATFULL  
CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 (vacuum distillation method for the separation of pentenenitrile isomers  
 prepared from)  
 RN 74-90-8 USPATFULL  
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL  
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 40 OF 60 USPATFULL on STN  
 ACCESSION NUMBER: 2007:69511 USPATFULL Full-text  
 TITLE: Sterically hindered chelate phosphinite-phosphite  
 ligand, catalyst, comprising at least one nickel(0)  
 complex stabilized by said ligand and method for  
 production of nitriles  
 INVENTOR(S): Bartsch, Michael, Neustadt, GERMANY, FEDERAL REPUBLIC  
 OF  
 Baumann, Robert, Mannheim, GERMANY, FEDERAL REPUBLIC OF  
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 Jungkamp, Tim, Kapellen, BELGIUM  
 Luyken, Hermann, Ludwigshafen, GERMANY, FEDERAL  
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 Scheidel, Jens, Hirschberg, GERMANY, FEDERAL REPUBLIC  
 OF  
 Siegel, Wolfgang, Limburgerhof, GERMANY, FEDERAL  
 REPUBLIC OF

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2007060766	A1	20070315	<--
APPLICATION INFO.:	US 2004-577138	A1	20041028	(10)
	WO 2004-EP12176		20041028	
			20060425	PCT 371 date

	NUMBER	DATE
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PRIORITY INFORMATION:	DE 2003-10350999	20031030
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	CONNOLLY BOVE LODGE & HUTZ LLP, P.O. BOX 2207, WILMINGTON, DE, 19899-2207, US	
NUMBER OF CLAIMS:	20	
EXEMPLARY CLAIM:	1	
LINE COUNT:	744	
CAS INDEXING IS AVAILABLE FOR THIS PATENT.		
AB	The invention relates to phosphinite phosphites I of formula 1, 2, 3, 4, 5 or 6 and mixtures thereof, wherein R1, R2, R4 independently represent an alkyl or alkylene group with 1 to 8 carbon atoms, provided that at least one of the groups R1, R2, R4 is different from H; R5 to R22 independently represent H, an alkyl or alkylene group with 1 to 8 carbon atoms; R3 is H, methyl or ethyl; X is F, Cl or CF.sub.3, if n=1 or 2 and X is H, if n=0.	
CAS INDEXING IS AVAILABLE FOR THIS PATENT.		
TI	Sterically hindered chelate phosphinite-phosphite ligand, catalyst, comprising at least one nickel(0) complex stabilized by said ligand and method for production of nitriles	
SUMM	Catalyst comprising at least one nickel(0) complex stabilized by a sterically demanding chelate phosphinite phosphite ligand, and preparation of nitriles	
SUMM	. . . appropriate processes for their preparation. Moreover, the present invention relates to the use of the transition metal complexes as a catalyst and to processes in the presence of such transition metal complexes as a catalyst.	
SUMM	Chelate phosphinite phosphites, nickel complexes having such phosphinite phosphite ligands and the use of such complexes as a catalyst are known.	
SUMM	. . . . It is desirable to improve the stability of the chelate phosphinite phosphite ligands to increase the on-stream time of the catalyst. Also desirable are an improvement in the selectivity of the catalyst, for example for 3-pentenitrile in the hydrocyanation of butadiene or for adiponitrile in the hydrocyanation of 3-pentenitrile, and an improvement. . .	
SUMM	. . . simple and economic manner, the hydrocyanation of unsaturated organic compounds with high stability, high reactivity and high selectivity of the catalyst.	
SUMM	The inventive transition metal complexes may be used as a catalyst, in particular as a homogeneous catalyst.	
SUMM	It has been found to be particularly advantageous to use the inventive transition metal complexes as a catalyst in the addition of hydrocyanic acid to olefinic double bonds, in particular those which are conjugated to a further olefinic. . . double bond, for example butadiene to obtain a mixture comprising 2-methyl-3-butenitrile and 3-pentenitrile. Equally advantageous is the use as a catalyst in the addition of hydrocyanic acid to olefinic double bonds which are not associated with a further olefinic double bond. . . .	
SUMM	It has likewise been found to be particularly advantageous to use the inventive transition metal complexes as a catalyst in the isomerization of organic nitriles, especially those in which the nitrile group is not conjugated to an olefinic double bond, for example 2-methyl-3-butenitrile to obtain 3-pentenitrile. Equally advantageous is also the use as a catalyst in the isomerization of organic nitriles in which the nitrile group is conjugated to an olefinic double bond.	



- SUMM . . . of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.tbd.N bonds by hydrocyanating a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst, wherein the hydrocyanation is effected in the presence of at least one of the above-described inventive systems.
- SUMM . . . under some circumstances, products are obtained in which a C.dbd.C double bond is conjugated with the C.tbd.N bond. "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1, VCH Weinheim, p. 479 discloses that conjugated 2-pentenitrile which is formed in the isomerization of. . . has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an unpretreated C.sub.4 cut also act as catalyst poisons for the first reaction step of adipic acid preparation, the monoaddition of hydrogen cyanide.
- SUMM Therefore, those components which give rise to catalyst poisons in the course of catalytic hydrocyanation, especially alkynes, 1,2-dienes and mixtures thereof, are optionally partly or fully removed from the hydrocarbon mixture. To remove these components, the C.sub.4 cut, before the addition of hydrogen cyanide, is preferably subjected to a catalytic partial hydrogenation. This partial hydrogenation is effected in the presence of a hydrogenation catalyst which is capable essentially of selectively hydrogenating alkynes and 1,2-dienes in addition to other dienes and monoolefins.
- SUMM Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the oxides which are customary for this purpose, in particular silicon oxides and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., and mixtures thereof. The supports used are preferably Al.sub.2O.sub.3, SiO.sub.2 and mixtures thereof. They are in particular the heterogeneous catalysts used in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906 which are fully incorporated here by way of reference. Further suitable Cu-based catalyst systems are sold by Dow Chemical as KLP catalyst.
- SUMM . . .
- a) charging a reactor with the hydrocarbon mixture, optionally a portion of the hydrogen cyanide and an inventive hydrocyanation catalyst which may optionally have been generated in situ, and also optionally a solvent,
- b) reacting the mixture at elevated. . .
- SUMM . . . reactor is charged before the start of the reaction with the part-hydrogenated C.sub.4 cut or butadiene, hydrogen cyanide, a hydrocyanation catalyst and also optionally a solvent. Suitable solvents are the preferably aromatic hydrocarbons which have been mentioned above for the preparation of the inventive catalysts, such as toluene and xylene, or tetrahydrofuran.
- SUMM . . . extracting, and the distillative workup of the remaining reaction mixture to remove the products of value and recover the still-active catalyst.
- SUMM . . . 3-pentenitrile and/or 4-pentenitrile and a very small fraction of conjugated 2-pentenitrile and 2-methyl-2-butenitrile which are in some cases active as catalyst poison.
3. Preparation of adiponitrile by adding hydrogen cyanide to the 3-pentenitrile formed in step 2 which has been. . .
- SUMM The inventive catalysts based on phosphinite ligands are also advantageously suitable for the positional and double bond isomerization in step 2 and/or the. . .
- SUMM Advantageously, the catalysts used in accordance with the invention do not only exhibit a high selectivity in relation to the monoaddition products obtained. . . of hydrogen cyanide in the hydrocyanation without noticeable deposition of inactive nickel(II) compounds, for

example nickel(II) cyanide. Unlike known hydrocyanation catalysts based on uncomplexed phosphine and phosphinite ligands, the catalysts containing a phosphinite phosphite I are thus suitable not only for continuous hydrocyanation processes in which a hydrogen cyanide excess. . . reaction mixture, but also for semicontinuous and batch processes in which there is generally a high hydrogen cyanide excess. The catalysts used in accordance with the invention and the processes for the hydrocyanation based on them thus generally have higher catalyst recycle rates and longer catalyst on-stream times than existing processes. In addition to better economic viability, this is also advantageous from the ecological viewpoint since the nickel cyanide formed from the active catalyst with hydrogen cyanide is highly poisonous and has to be worked up or disposed of at high cost.

SUMM The addition of hydrocyanic acid to an olefinic double bond in the presence of an inventive catalyst system, especially the addition to butadiene, a butadiene or to 3-pentenitrile, 4-pentenitrile or mixtures of such pentenenitriles, or the isomerization of organic nitriles in the presence of an inventive catalyst system, especially the isomerization of 2-methyl-3-butenitrile to 3-pentenitrile, may advantageously be carried out in the presence of one or more Lewis acids as promoters which influence the activity, selectivity or both of the inventive catalyst system. Useful promoters are inorganic and organic compounds in which the cation is selected from the group consisting of scandium, . . . group. U.S. Pat. No. 4,874,884 describes how synergistically active combinations of promoters, may be selected in order to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3 and (C.sub.6H.sub.5).sub.3SnZ where Z is CF.sub.3SO.sub.3, CH.sub.3C.sub.6H.sub.4SO.sub.3 or (C.sub.6H.sub.5).sub.3BCN.

SUMM The molar ratio of promoter to nickel in the catalyst system may be between 1:16 and 50:1.

SUMM . . . by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

SUMM . . . by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

SUMM . . . by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

SUMM . . . by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

DETD All examples were carried out under a protective gas atmosphere of argon. The advantageous specification of the starting materials BD, HCN, 3PN and 2M3BN can be taken from WO 03/045552.

DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3',5,5'-tetramethylbiphenol and 160 mmol of triethylamine are initially charged at -15° C. in 120 ml of. . .

DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3',5,5',6,6'-hexamethylbiphenol and 160 mmol of triethylamine are initially charged at -15° C. in 120 ml of. . .

DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3'-diisopropyl-6,6'-dimethylbiphenol and 44 mmol of diphenylchlorophosphine are initially charged at -15° C. in 120 ml of. . .

CLM What is claimed is:

7. The use of a transition metal complex as claimed in claim 4 as a catalyst.

10. A process comprising adding hydrocyanic acid to an olefinic double bond in the presence of a catalyst, wherein the catalyst is a transition metal complex as claimed in claim 5.

13. A process comprising isomerizing organic nitrites in the presence of a catalyst, wherein the catalyst used is a transition metal complex as claimed in claim 5.

IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,

1,3-Butadiene, reactions

(hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)

IT 4635-87-4P, 3-Pentenitrile

(isomerization, hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)

TI Sterically hindered chelate phosphinite-phosphite ligand, catalyst, comprising at least one nickel(0) complex stabilized by said ligand and method for production of nitriles|

PI US 2007060766 A1 20070315 <--|

SUMM Catalyst comprising at least one nickel(0) complex stabilized by a sterically demanding chelate phosphinite phosphite ligand, and preparation of nitriles

SUMM The present invention relates to novel phosphinite phosphites, in particular chelate phosphinite phosphites, and to a process for their preparation. The present invention further provides their use as a ligand in transition metal complexes, novel transition metal complexes and appropriate processes for their preparation. Moreover, the present invention relates to the use of the transition metal complexes as a catalyst and to processes in the presence of such transition metal complexes as a catalyst.

SUMM Chelate phosphinite phosphites, nickel complexes having such phosphinite phosphite ligands and the use of such complexes as a catalyst are known.

SUMM U.S. Pat. No. 5,693,843 and 5,523,453 describe processes for hydrocyanating unsaturated organic compounds and the isomerization of nitriles in the presence of nickel(0) complexes having chelate phosphinite phosphites as a ligand. It is desirable to improve the stability of the chelate phosphinite phosphite ligands to increase the on-stream time of the catalyst. Also desirable are an improvement in the selectivity of the catalyst, for example for 3-pentenitrile in the hydrocyanation of butadiene or for adiponitrile in the hydrocyanation of 3-pentenitrile, and an improvement in the space-time yield.

SUMM It is an object of the present invention to provide phosphinite phosphites which are suitable as chelate phosphinite phosphites and enable, in a technically simple and economic manner, the hydrocyanation of unsaturated organic compounds with high stability, high reactivity and high selectivity of the catalyst.

SUMM The inventive transition metal complexes may be used as a catalyst, in particular as a homogeneous catalyst.

SUMM It has been found to be particularly advantageous to use the inventive

transition metal complexes as a catalyst in the addition of hydrocyanic acid to olefinic double bonds, in particular those which are conjugated to a further olefinic double bond, for example butadiene to obtain a mixture comprising 2-methyl-3-butenitrile and 3-pentenitrile. Equally advantageous is the use as a catalyst in the addition of hydrocyanic acid to olefinic double bonds which are not associated with a further olefinic double bond, for example 3-pentenitrile or 4-pentenitrile or mixtures thereof, preferably 3-pentenitrile, to obtain adiponitrile, or 3-pentenoic ester or 4-pentenoic ester or mixtures thereof, preferably 3-pentenoic ester, to obtain 5-cyanovaleric ester.

SUMM It has likewise been found to be particularly advantageous to use the inventive transition metal complexes as a catalyst in the isomerization of organic nitriles, especially those in which the nitrile group is not conjugated to an olefinic double bond, for example 2-methyl-3-butenitrile to obtain 3-pentenitrile. Equally advantageous is also the use as a catalyst in the isomerization of organic nitriles in which the nitrile group is conjugated to an olefinic double bond.

SUMM The invention further provides a process for preparing mixtures of monoolefinic C.sub.5-mono nitriles having nonconjugated C.dbd.C and C.tbd.N bonds by hydrocyanating a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst, wherein the hydrocyanation is effected in the presence of at least one of the above-described inventive systems.

SUMM C.sub.4 cuts are optionally substantially freed of alkynes, e.g. propyne or butyne, of 1,2-dienes, e.g. propadiene, and of alkenynes, e.g. vinylacetylene. Otherwise, under some circumstances, products are obtained in which a C.dbd.C double bond is conjugated with the C.tbd.N bond. "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1, VCH Weinheim, p. 479 discloses that conjugated 2-pentenitrile which is formed in the isomerization of 2-methyl-3-butenitrile and 3-pentenitrile acts as a reaction inhibitor for the secondary addition of hydrogen cyanide to adiponitrile. It has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an unpreacted C.sub.4 cut also act as catalyst poisons for the first reaction step of adipic acid preparation, the monoaddition of hydrogen cyanide.

SUMM Therefore, those components which give rise to catalyst poisons in the course of catalytic hydrocyanation, especially alkynes, 1,2-dienes and mixtures thereof, are optionally partly or fully removed from the hydrocarbon mixture. To remove these components, the C.sub.4 cut, before the addition of hydrogen cyanide, is preferably subjected to a catalytic partial hydrogenation. This partial hydrogenation is effected in the presence of a hydrogenation catalyst which is capable essentially of selectively hydrogenating alkynes and 1,2-dienes in addition to other dienes and monoolefins.

SUMM Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the oxides which are customary for this purpose, in particular silicon oxides and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., and mixtures thereof. The supports used are preferably Al.sub.2O.sub.3, SiO.sub.2 and mixtures thereof. They are in particular the heterogeneous catalysts used in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906 which

are fully incorporated here by way of reference. Further suitable Cu-based catalyst systems are sold by Dow Chemical as KLP catalyst.

SUMM The semicontinuous process comprises:

- a) charging a reactor with the hydrocarbon mixture, optionally a portion of the hydrogen cyanide and an inventive hydrocyanation catalyst which may optionally have been generated in situ, and also optionally a solvent,
- b) reacting the mixture at elevated temperature and elevated pressure by feeding in hydrogen cyanide in semicontinuous mode in accordance with its consumption,
- c) completing the reaction by continued reaction and subsequent workup.

SUMM The pressure-rated reactor is charged before the start of the reaction with the part-hydrogenated C.sub.4 cut or butadiene, hydrogen cyanide, a hydrocyanation catalyst and also optionally a solvent. Suitable solvents are the preferably aromatic hydrocarbons which have been mentioned above for the preparation of the inventive catalysts, such as toluene and xylene, or tetrahydrofuran.

SUMM To complete the conversion, the reaction time may be followed by a continued reaction time of from 0 minutes to about 5 hours, preferably from about 1 hour to 3.5 hours, in which no more hydrogen cyanide is fed into the autoclave. In this time, the temperature is left substantially constant at the reaction temperature set beforehand. The workup is effected by common methods and comprises the removal of the unconverted 1,3-butadiene and of the unconverted hydrogen cyanide, for example by washing or extracting, and the distillative workup of the remaining reaction mixture to remove the products of value and recover the still-active catalyst.

SUMM Generally, the preparation of adiponitrile from a butadiene-containing mixture by adding 2 molar equivalents of hydrogen cyanide can be divided into three steps:

1. Preparation of C.sub.5 monoolefin mixtures having nitrile function.
2. isomerization of the 2-methyl-3-butenenitrile present in these mixtures to 3-pentenitrile and isomerization of the 3-pentenitrile formed in this way and already present in the mixtures from step 1 to different n-pentenitriles. This should form a very high fraction of 3-pentenitrile and/or 4-pentenitrile and a very small fraction of conjugated 2-pentenitrile and 2-methyl-2-butenenitrile which are in some cases active as catalyst poison.
3. Preparation of adiponitrile by adding hydrogen cyanide to the 3-pentenitrile formed in step 2 which has been isomerized beforehand in situ to 4-pentenitrile. The by-products which occur are, for example, 2-methylglutarodinitrile from the Markovnikov addition of hydrogen cyanide to 4-pentenitrile or the anti-Markovnikov addition of hydrogen cyanide to 3-pentenitrile and ethylsuccinonitrile from the Markovnikov addition of hydrogen cyanide to 3-pentenitrile.

SUMM The inventive catalysts based on phosphinite ligands are also advantageously suitable for the positional and double bond isomerization in step 2 and/or the secondary addition of hydrogen cyanide in step 3.

SUMM Advantageously, the catalysts used in accordance with the invention do not only exhibit a high selectivity in relation to the monoaddition products obtained in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures, but they may also be admixed with an excess of

hydrogen cyanide in the hydrocyanation without noticeable deposition of inactive nickel(II) compounds, for example nickel(II) cyanide. Unlike known hydrocyanation catalysts based on uncomplexed phosphine and phosphinite ligands, the catalysts containing a phosphinite phosphite I are thus suitable not only for continuous hydrocyanation processes in which a hydrogen cyanide excess is generally effectively avoided in the reaction mixture, but also for semicontinuous and batch processes in which there is generally a high hydrogen cyanide excess. The catalysts used in accordance with the invention and the processes for the hydrocyanation based on them thus generally have higher catalyst recycle rates and longer catalyst on-stream times than existing processes. In addition to better economic viability, this is also advantageous from the ecological viewpoint since the nickel cyanide formed from the active catalyst with hydrogen cyanide is highly poisonous and has to be worked up or disposed of at high cost.

**SUMM** The addition of hydrocyanic acid to an olefinic double bond in the presence of an inventive catalyst system, especially the addition to butadiene, a butadiene or to 3-pentenitrile, 4-pentenitrile or mixtures of such pentenenitriles, or the isomerization of organic nitriles in the presence of an inventive catalyst system, especially the isomerization of 2-methyl-3-butenitrile to 3-pentenitrile, may advantageously be carried out in the presence of one or more Lewis acids as promoters which influence the activity, selectivity or both of the inventive catalyst system. Useful promoters are inorganic and organic compounds in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include ZnBr.sub.2, ZnI.sub.2, ZnCl.sub.2, ZnSO.sub.4, CuCl.sub.2, CuCl, Cu(O.sub.3SCF.sub.3).sub.2, CoCl.sub.2, Col.sub.2, FeI.sub.2, FeCl.sub.3, FeCl.sub.2(THF).sub.2, TiCl.sub.4(THF).sub.2, TiCl.sub.4, TiCl.sub.3, ClTi(O-iso-Pr).sub.3, MnCl.sub.2, ScCl.sub.3, AlCl.sub.3, (C.sub.2H.sub.5)AlCl.sub.2, (C.sub.2H.sub.5).sub.2AlCl, (C.sub.2H.sub.5).sub.3Al.sub.2Cl.sub.3, (C.sub.8H.sub.17)AlCl.sub.2, (C.sub.8H.sub.17).sub.2AlCl, (iso-C.sub.4H.sub.9).sub.2AlCl, Ph.sub.2AlCl, PhAlCl.sub.2, ReCl.sub.5, ZrCl.sub.4, ZrCl.sub.2, NbCl.sub.5, VCl.sub.3, CrCl.sub.2, MoCl.sub.5, YCl.sub.3, CdCl.sub.2, LaCl.sub.3, Er(O.sub.3SCF.sub.3).sub.3, Yb(O.sub.2CCF.sub.3).sub.3, SmCl.sub.3, B(C.sub.6H.sub.5).sub.3, TaCl.sub.5, as generally described in U.S. Pat. No. 6,171,996 B1. Preferred promoters are also described in U.S. Pat. No. 3,496,217, U.S. Pat. No. 3,496,218 and U.S. Pat. No. 4,774,353. These include metal salts such as ZnCl.sub.2, Col.sub.2 and SnCl.sub.2, and organometallic compounds such as RAlCl.sub.2, R.sub.3SnO.sub.3SCF.sub.3, and R.sub.3B, where R is an alkyl group or aryl group. U.S. Pat. No. 4,874,884 describes how synergistically active combinations of promoters, may be selected in order to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3 and (C.sub.6H.sub.5).sub.3SnZ where Z is CF.sub.3SO.sub.3, CH.sub.3CO.sub.6H.sub.4SO.sub.3 or (C.sub.6H.sub.5).sub.3BCN.

**SUMM** The molar ratio of promoter to nickel in the catalyst system may be between 1:16 and 50:1.

**SUMM** A further advantageous embodiment of the hydrocyanation and isomerization can be taken from U.S. Pat. No. 5,981,772, whose contents are fully incorporated in the present application by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

- SUMM A further advantageous embodiment of the hydrocyanation and isomerization can be taken from U.S. Pat. No. 6,127,567, whose contents are fully incorporated in the present application by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.
- SUMM A further advantageous embodiment of the hydrocyanation can be taken from U.S. Pat. No. 5,693,843, whose contents are fully incorporated in the present application by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.
- SUMM A further advantageous embodiment of the hydrocyanation can be taken from U.S. Pat. No. 5,523,453, whose contents are fully incorporated in the present application by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.
- DETD All examples were carried out under a protective gas atmosphere of argon. The advantageous specification of the starting materials BD, HCN, 3PN and 2M3BN can be taken from WO 03/045552.
- DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3',5,5'-tetramethylbiphenol and 160 mmol of triethylamine are initially charged at -15° C. in 120 ml of toluene in a 500 ml flask. At this temperature, 44 mmol of diphenylchlorophosphine dissolved in 40 ml of toluene are added dropwise within 40 min. The mixture is stirred at -15° C. for a further 6 h. At -15° C., 40 mmol of di-o-cresyl chlorophosphite dissolved in 40 ml of toluene are added dropwise to the mixture. The mixture is allowed to come to room temperature and stirred for a further 15 h. The mixture is filtered and the filtrate fully concentrated. 25.3 g of product are obtained.  
.sup.31P NMR (C.sub.6D.sub.6): 133.5 ppm and 112.8 ppm; bisphosphinite impurities 112.5 ppm.
- DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3',5,5',6,6'-hexamethylbiphenol and 160 mmol of triethylamine are initially charged at -15° C. in 120 ml of toluene in a 500 ml flask. At this temperature, 44 mmol of diphenylchlorophosphine dissolved in 40 ml of toluene are added dropwise within 40 min. The mixture is stirred at -15° C. for a further 6 h. At -15° C., 40 mmol of di-o-cresyl chlorophosphite dissolved in 40 ml of toluene are added dropwise to the mixture. The mixture is allowed to come to room temperature and stirred for a further 15 h. The mixture is filtered and the filtrate fully concentrated. 21.5 g of product are obtained.  
.sup.31P NMR (C.sub.6D.sub.6): 134.7 ppm and 110.6 ppm.
- DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3'-diisopropyl-6,6'-dimethylbiphenol and 44 mmol of diphenylchlorophosphine are initially charged at -15° C. in 120 ml of toluene in a 500 ml flask. At this temperature, 160 mmol of triethylamine dissolved in 40 ml of toluene are added dropwise within 40 min. The mixture is stirred at -15° C. for a further 6 h. At -15° C., 40 mmol of di-o-cresyl chlorophosphite dissolved in 40 ml of toluene are added dropwise to the mixture. The mixture is allowed to come to room temperature and stirred for a further 15 h. The mixture is filtered and the filtrate fully concentrated. 21.5 g of product are obtained.  
.sup.31P NMR (C.sub.6D.sub.6): 132.5 ppm and 113.5 ppm.
7. The use of a transition metal complex as claimed in claim 4 as a catalyst.

10. A process comprising adding hydrocyanic acid to an olefinic double bond in the presence of a catalyst, wherein the catalyst is a transition metal complex as claimed in claim 5.

13. A process comprising isomerizing organic nitrites in the presence of a catalyst, wherein the catalyst used is a transition metal complex as claimed in claim 5.

IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,

1,3-Butadiene, reactions

(hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)

IT 4635-87-4P, 3-Pentenitrile

(isomerization, hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)

IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,

1,3-Butadiene, reactions

(hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)

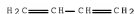
RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenitrile

(isomerization, hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)

RN 4635-87-4 USPATFULL

CN 3-Pentenitrile (CA INDEX NAME)





10/586490

TITLE: Process of synthesis of compounds having nitrile functions from ethylenically unsaturated compounds

INVENTOR(S): Rosier, Cecile, Soucieu En Jarrest, FRANCE  
Marion, Philippe, Vernaison, FRANCE  
Bourgeois, Damien, Lyon, FRANCE

PATENT ASSIGNEE(S): RHODIA POLYAMIDE INTERMEDIATES (non-U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 2006252955	A1	20061109
APPLICATION INFO.:	US 2006-475210	A1	20060627 (11)
RELATED APPLN. INFO.:	Division of Ser. No. US 2003-353912, filed on 30 Jan 2003, GRANTED, Pat. No. US 7084293		

	NUMBER	DATE
PRIORITY INFORMATION:	FR 2002-16550	20021223
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	BUCHANAN, INGERSOLL & ROONEY PC, POST OFFICE BOX 1404, ALEXANDRIA, VA, 22313-1404, US	
NUMBER OF CLAIMS:	24	
EXEMPLARY CLAIM:	1	
LINE COUNT:	699	

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A process of hydrocyanation of diolefins such as butadiene is carried out in the presence of a catalytic system comprising a transition metal and mono- and pluri-dentate organophosphorus ligands. The reaction medium containing branched nitrites subsequently is isomerized in the absence of hydrogen cyanide.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

DETD . . . the context of discontinuous performance, there can be charged into a reactor, purged beforehand with an inert gas (such as nitrogen, argon) either a solution containing the whole or a portion of the various constituents, such as the compound to undergo hydrocyanation, . . .

DETD If need be, a slight flushing of the reactor with an inert gas such as nitrogen or argon can be performed in order to expel the hydrogen cyanide which could still be present.

IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, Butadiene, reactions 110-59-8, Valeronitrile 110-83-8, Cyclohexene, reactions 111-69-3, Adiponitrile 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, Pentene-4-nitrile 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butenenitrile 4553-62-2, 2-Methyl glutaronitrile 4635-87-4, 3-Pentenitrile 13284-42-9, 2-Pentenitrile 16529-56-9, 2-Methyl-3-butenenitrile 17611-82-4, 2-Ethyl succinonitrile 25013-15-4, Methylstyrene 26588-32-9, Vinyl naphthalene (process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

DETD In the context of discontinuous performance, there can be charged into a reactor, purged beforehand with an inert gas (such as nitrogen, argon) either a solution containing the whole or a portion of the various constituents, such as the compound to undergo hydrocyanation, the compounds of formulas (I) and (II), the transition metal compound, the possible reducing agent and solvent; or the said constituents

separately. The reactor is generally then brought to the chosen temperature. The hydrogen cyanide is then introduced, preferably in a continuous and regular manner.

DETD If need be, a slight flushing of the reactor with an inert gas such as nitrogen or argon can be performed in order to expel the hydrogen cyanide which could still be present.

IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, Butadiene, reactions 110-59-8, Valeronitrile 110-83-8, Cyclohexene, reactions 111-69-3, Adiponitrile 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, Pentene-4-nitrile 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butenenitrile 4553-62-2, 2-Methyl glutaronitrile 4635-87-4, 3-Pentenitrile 13284-42-9, 2-Pentenitrile 16529-56-9, 2-Methyl-3-butenenitrile 17611-82-4, 2-Ethyl succinonitrile 25013-15-4, Methylstyrene 26588-32-9, Vinyl naphthalene (process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, Butadiene, reactions 4635-87-4, 3-Pentenitrile (process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

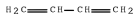
RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



RN 4635-87-4 USPATFULL

CN 3-Pentenitrile (CA INDEX NAME)



L88 ANSWER 42 OF 60 USPATFULL on STN

ACCESSION NUMBER: 2005:105739 USPATFULL Full-text

TITLE: Phosphonites, use thereof as ligand in transition metal complexes and method for production of nitriles

INVENTOR(S): Bartsch, Michael, Neustadt, GERMANY, FEDERAL REPUBLIC OF

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 BASF Aktiengesellschaft, Ludwigshafen, GERMANY, FEDERAL  
 REPUBLIC OF (non-U.S. corporation)

## PATENT ASSIGNEE(S):

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2005090678	A1	20050428	<--
	US 7067685	B2	20060627	
APPLICATION INFO.:	US 2003-491918	A1	20021004	(10)
	WO 2002-EP11107		20021004	

	NUMBER	DATE
PRIORITY INFORMATION:	DE 2001-10150281	20011012
	DE 2003-10207165	20020220
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	KEIL & WEINKAUF, 1350 CONNECTICUT AVENUE, N.W., WASHINGTON, DC, 20036, US	
NUMBER OF CLAIMS:	14	
EXEMPLARY CLAIM:	1	
LINE COUNT:	786	

## CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention relates to phosphinites I of formulae (1) or (2), in which R<sub>1</sub>, R<sub>2</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> independently represent hydrogen, an alkyl or alkylene group having 1 to 8 carbon atoms or an alkoxy group having 1 to 8 carbon atoms; R<sub>3</sub> is H or methyl; R<sub>4</sub> is i-propyl or t-butyl; X is F, Cl or CF<sub>3</sub>.sub.3 and n is 1 or 2. ##STR1##

## CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . use as ligands in transition metal complexes, novel transition metal complexes, a process for preparing the complexes, their use as catalyst and processes carried out in the presence of such transition metal complexes as catalyst.

SUMM Chelating phosphonites, nickel complexes containing such phosphonites as ligands and the use of such complexes as catalysts are known.

SUMM . . . It would be desirable to improve the stability of the chelating phosphonite ligands to increase the operating life of the catalyst. Furthermore, an improvement in the selectivity of the catalyst, for example to 3-pentenitrile in the hydrocyanation of butadiene or to adiponitrile in the hydrocyanation of 3-pentenitrile, and an improvement. . .

SUMM . . . provide phosphonites which are suitable as chelating phosphonites and display high, stability, high reactivity and high selectivity when used as catalysts in the hydrocyanation of unsaturated organic compounds and make it possible for such hydrocyanations to be carried out in a. . .

SUMM . . . them, their use as ligands in transition metal complexes, novel transition metal complexes, processes for preparing them, their use as catalysts and processes carried out in the presence of such

transition metal complexes as catalysts.

SUMM The transition metal complexes of the present invention can be used as catalysts, in particular as homogeneous catalysts.

SUMM It has been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the addition of hydrocyanic acid onto olefinic double bonds, in particular double bonds which are conjugated with a further. . . a mixture comprising 2-methyl-3-butenitrile and 3-pentenitrile. It is equally advantageous to use the transition metal complexes of the invention as catalysts in the addition of hydrocyanic acid onto olefinic double bond which are not conjugated with a further olefinic double bond, . . .

SUMM It has likewise been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles, in particular ones in which the nitrile group is not conjugated with an olefinic. . . of 2-methyl-3-butenitrile to give 3-pentenitrile. It is equally advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles in which the nitrile group is conjugated with an olefinic double bond.

SUMM . . . hydrocarbon mixture in the presence of at least one of the above described systems according to the present invention as catalyst.

SUMM . . . which a C.dbd.C double bond is conjugated with the C.dbd.N bond are sometimes obtained. It is known from "Applied Homogeneous Catalysis with Organometallic Compounds", vol. 1, VCH Weinheim, p. 479, that the conjugated 2-pentenitrile formed in the isomerization of 2-methyl-3-butenitrile and. . . has been found that the abovementioned conjugated nitrites obtained in the hydrocyanation of an unpretreated C.sub.4 fraction also act as catalyst poisons for the first reaction step of the preparation of adipic acid, namely the monoaddition of hydrogen cyanide.

SUMM For this reason, it may be useful to free the hydrocarbon mixture partly or completely of components which form catalyst poisons in the catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof. To remove these components, the C.sub.4 fraction is subjected to a catalytic partial hydrogenation before the addition of hydrogen cyanide. This partial hydrogenation is carried out in the presence of a hydrogenation catalyst which is capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.

SUMM Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the customary oxides, in particular silicon and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., and mixtures thereof. Preference is given to using Al.sub.2O.sub.3, SiO.sub.2 and mixtures thereof as supports. In particular, the heterogeneous catalysts used are those described in U.S. Pat. No. 4,587,369.; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on Cu are marketed by Dow Chemical as KLP catalyst.

SUMM . . .

- a) charging a reactor with the hydrocarbon mixture, if desired part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired produced in situ, and, if desired, a solvent,
- b) reacting the mixture. . .

SUMM The pressure-rated reactor is charged with the partially hydrogenated C.sub.4 fraction or butadiene, hydrogen cyanide, a hydrocyanation catalyst and, if desired, a solvent prior to commencement of the

reaction. Suitable solvents are those mentioned above for the preparation of the catalysts of the present invention, preferably aromatic hydrocarbons such as toluene and xylene, or tetrahydrofuran.

SUMM . . . extraction, and fractionally distilling the remaining reaction mixture to separate off the products of value and recover the still active catalyst.

SUMM . . . high proportion of 3-pentenitrile or 4-pentenitrile and a very small proportion of conjugated 2-pentenitrile and 2-methyl-2-butenitrile, which may act as catalyst poisons, should be formed.

SUMM The novel catalysts based on phosphonite ligands can also be used advantageously for the structural isomerization and double bond isomerization in step 2. . .

SUMM Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation. . . excess of hydrogen cyanide without appreciable deposition of inactive nickel(II) compounds, e.g. nickel(II) cyanide, occurring. In contrast to known hydrocyanation catalysts based on uncomplexed phosphine and phosphite ligands, the catalysts comprising a phosphonite I are thus suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide. . . but also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. The catalysts used according to the present invention and the hydrocyanation processes based on them generally display higher catalyst recycle rates and longer catalyst operating times than do known processes. Apart from the economic aspect, this is also advantageous for ecological reasons since the nickel cyanide formed by reaction of the active catalyst with hydrogen cyanide is highly toxic and has to be worked up or disposed of at high cost.

SUMM The addition of hydrocyanic acid onto an olefinic double bond in the presence of a catalyst system according to the present invention, in particular the addition onto butadiene or onto 3-pentenitrile, 4-pentenitrile or a mixture of such pentenenitriles or the isomerization of organic nitriles in the presence of a catalyst system according to the present invention, in particular the isomerization of 2-methyl-3-butenitrile to 3-pentenitrile, can advantageously be carried out in the presence of one or more Lewis acids as promoters which influence the activity, selectivity or both of the catalyst system of the present invention. Possible promoters are inorganic and organic compounds in which the cation is selected from the. . . group or aryl group. U.S. Pat. No. 4,874,884 describes the selection of synergistically effective combinations of promoters to increase the catalytic activity of the catalyst system. Preferred promoters include  $\text{CdCl.sub.2}$ ,  $\text{FeCl.sub.2}$ ,  $\text{ZnCl.sub.2}$ ,  $\text{B(C.sub.6H.sub.5).sub.3}$  and  $\text{(C.sub.6H.sub.5).sub.3SnZ}$ , where Z is  $\text{CF.sub.3SO.sub.3}$ ,  $\text{CH.sub.3CO.sub.6H.sub.4SO.sub.3}$  or  $\text{(C.sub.6H.sub.5).sub.3BCN}$ .

SUMM The molar ratio of promoter to nickel in the catalyst system can be in the range from 1:16 to 50:1.

SUMM . . . may be found in U.S. Pat. No. 5,981,772, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

SUMM . . . may be found in U.S. Pat. No. 6,127,567, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

SUMM . . . may be found in U.S. Pat. No. 5,693,843, whose contents are

hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

- SUMM . . . may be found in U.S. Pat. No. 5,523,453, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.
- DETD All examples were carried out under a protective argon atmosphere.
- DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 94 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes, 60 minutes and 150 minutes. . . .
- DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 142 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and after 60 minutes and. . . .
- DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 85 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 45 minutes and 60 minutes and analyzed. . . .
- DETD . . . to this mixture and the mixture was stirred for a further 5 minutes. 128 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and after 60 minutes and. . . .
- DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 106 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed. . . .
- DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 123 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed. . . .
- DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 127 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed. . . .
- DETD Virtually no temperature increase occurs. This means that the catalyst is not very active.
- DETD Virtually no temperature increase occurs. This means that the catalyst is not very active.
- CLM What is claimed is:
- . . . them, their use as ligands in transition metal complexes, novel transition metal complexes, processes for preparing them, their use as catalysts and processes carried out in the presence of such transition metal complexes as catalysts.
7. The use of a transition metal complex as claimed in claim 4 or 5 as catalyst.
8. The use as claimed in claim 7 as catalyst for the addition of hydrocyanic acid onto an olefinic double bond.
9. The use as claimed in claim 7 as catalyst for the isomerization of organic nitriles.
- . . . an olefinic double bond in the presence of a transition metal complex as claimed in claim 4 or 5 as catalyst.

. . . isomerization of organic nitrites in the presence of a transition metal complex as claimed in claim 4 or 5 as catalyst.

IT 106-99-0, 1,3-Butadiene, reactions  
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)

IT 4635-87-4P, 3-Pentenitrile  
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)

IT 592-51-8P, 4-Pentenitrile 16529-66-1P, trans-3-Pentenitrile  
16545-78-1P, cis-3-Pentenitrile 20068-02-4P,  
cis-2-Methyl-2-butenitrile 26294-98-4P, trans-2-Pentenitrile  
28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenitrile  
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)

IT 74-98-9, Hydrogen cyanide, reactions  
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)

PI US 2005090678 A1 20050428 <--|  
US 7067685 B2 20060627|

SUMM The present invention relates to novel phosphonites, in particular chelating phosphonites, methods of preparing them, their use as ligands in transition metal complexes, novel transition metal complexes, a process for preparing the complexes, their use as catalyst and processes carried out in the presence of such transition metal complexes as catalyst.

SUMM Chelating phosphonites, nickel complexes containing such phosphonites as ligands and the use of such complexes as catalysts are known.

SUMM WO 99/13983 and WO 99/64155 describe a process for the hydrocyanation of unsaturated organic compounds and the isomerization of nitrites in the presence of nickel(0) complexes containing chelating phosphonites as ligands. The chelating phosphonites described have good stability under the corresponding reaction conditions. It would be desirable to improve the stability of the chelating phosphonite ligands to increase the operating life of the catalyst. Furthermore, an improvement in the selectivity of the catalyst, for example to 3-pentenitrile in the hydrocyanation of butadiene or to adiponitrile in the hydrocyanation of 3-pentenitrile, and an improvement in the space-time yield are desirable.

SUMM It is an object of the present invention to provide phosphonites which are suitable as chelating phosphonites and display high, stability, high reactivity and high selectivity when used as catalysts in the hydrocyanation of unsaturated organic compounds and make it possible for such hydrocyanations to be carried out in a technically simple and economical manner.

SUMM We have found that this object is achieved by phosphonites I of the formula 1 or 2 ##STR2## where

R1, R2, R5, R6, R7, R8, R9 are each, independently of one another, hydrogen, an alkyl or alkylene group having from 1 to 8 carbon atoms or an alkoxy group having from 1 to 8 carbon atoms,  
R3 is H or methyl,  
R4 is i-propyl or t-butyl,  
X is F, Cl or CF.sub.3  
n is 1 or 2,

and also methods of preparing them, their use as ligands in transition metal complexes, novel transition metal complexes, processes for preparing them, their use as catalysts and processes carried out in the presence of such transition metal complexes as catalysts.

SUMM The transition metal complexes of the present invention can be used as catalysts, in particular as homogeneous catalysts.

SUMM It has been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the addition of hydrocyanic acid onto olefinic double bonds, in particular double bonds which are conjugated with a further olefinic double bond, for example onto a double bond of butadiene to give a mixture comprising 2-methyl-3-butenitrile and 3-pentenitrile. It is equally advantageous to use the transition metal complexes of the invention as catalysts in the addition of hydrocyanic acid onto olefinic double bond which are not conjugated with a further olefinic double bond, for example onto the double bond of 3-pentenitrile or 4-pentenitrile or mixtures thereof, preferably 3-pentenitrile, to give adiponitrile, or onto 3-pentenoic esters or 4-pentenoic esters or mixtures thereof, preferably 3-pentenoic esters, to give 5-cyanovaleric esters.

SUMM It has likewise been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles, in particular ones in which the nitrile group is not conjugated with an olefinic double bond, for example the isomerization of 2-methyl-3-butenitrile to give 3-pentenitrile. It is equally advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles in which the nitrile group is conjugated with an olefinic double bond.

SUMM The invention also provides a process for preparing mixtures of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of at least one of the above described systems according to the present invention as catalyst.

SUMM C.sub.4 fractions are, if desired, substantially freed of alkynes, e.g. propyne or butyne, of 1,2-dienes, e.g. propadiene, and of alkenynes, e.g. vinylacetylene. Otherwise, products in which a C.dbd.C double bond is conjugated with the C.dbd.N bond are sometimes obtained. It is known from "Applied Homogeneous Catalysis with Organometallic Compounds", vol. 1, VCH Weinheim, p. 479, that the conjugated 2-pentenitrile formed in the isomerization of 2-methyl-3-butenitrile and 3-pentenitrile acts as a reaction inhibitor for the second addition of hydrogen cyanide to form adiponitrile. It has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an untreated C.sub.4 fraction also act as catalyst poisons for the first reaction step of the preparation of adipic acid, namely the monoaddition of hydrogen cyanide.

SUMM For this reason, it may be useful to free the hydrocarbon mixture partly or completely of components which form catalyst poisons in the catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof. To remove these components, the C.sub.4 fraction is subjected to a catalytic partial hydrogenation before the addition of hydrogen cyanide. This partial hydrogenation is carried out in the presence of a hydrogenation catalyst which is capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and



monoolefins.

SUMM Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the customary oxides, in particular silicon and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., and mixtures thereof. Preference is given to using Al.sub.2O.sub.3, SiO.sub.2 and mixtures thereof as supports. In particular, the heterogeneous catalysts used are those described in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on Cu are marketed by Dow Chemical as KLP catalyst.

SUMM The semicontinuous process comprises:

- a) charging a reactor with the hydrocarbon mixture, if desired part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired produced in situ, and, if desired, a solvent,
- b) reacting the mixture at elevated temperature and superatmospheric pressure, with hydrogen cyanide being fed in at the rate at which it is consumed,
- c) completing the conversion by a period of after-reaction and subsequently working up the mixture.

SUMM The pressure-rated reactor is charged with the partially hydrogenated C.sub.4 fraction or butadiene, hydrogen cyanide, a hydrocyanation catalyst and, if desired, a solvent prior to commencement of the reaction. Suitable solvents are those mentioned above for the preparation of the catalysts of the present invention, preferably aromatic hydrocarbons such as toluene and xylene, or tetrahydrofuran.

SUMM To complete the conversion, the reaction time can be followed by an after-reaction time of up to about 5 hours, preferably from about 1 hour to 3.5 hours, during which no more hydrogen cyanide is fed into the autoclave. During this time, the temperature is kept essentially constant at the reaction temperature set during the addition of hydrogen cyanide. Work-up is carried out by customary methods and comprises separating off the unreacted 1,3-butadiene and the unreacted hydrogen cyanide, e.g. by washing or extraction, and fractionally distilling the remaining reaction mixture to separate off the products of value and recover the still active catalyst.

SUMM 2. Isomerization of the 2-methyl-3-butenenitrile present in these mixtures to form 3-pentenitrile and isomerization of the 3-pentenitrile formed in this way and the 3-pentenitrile already present in the mixtures from step 1 to form various n-pentenitriles. A very high proportion of 3-pentenitrile or 4-pentenitrile and a very small proportion of conjugated 2-pentenitrile and 2-methyl-2-butenenitrile, which may act as catalyst poisons, should be formed.

SUMM The novel catalysts based on phosphonite ligands can also be used advantageously for the structural isomerization and double bond isomerization in step 2 and/or the second addition of hydrogen cyanide in step 3.

SUMM Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures but they can also be admixed with an excess of hydrogen cyanide without appreciable deposition of inactive nickel(II) compounds, e.g.

nickel(II) cyanide, occurring. In contrast to known hydrocyanation catalysts based on uncomplexed phosphine and phosphite ligands, the catalysts comprising a phosphonite I are thus suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide in the reaction mixture can generally be effectively avoided but also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. The catalysts used according to the present invention and the hydrocyanation processes based on them generally display higher catalyst recycle rates and longer catalyst operating times than do known processes. Apart from the economic aspect, this is also advantageous for ecological reasons since the nickel cyanide formed by reaction of the active catalyst with hydrogen cyanide is highly toxic and has to be worked up or disposed of at high cost.

SUMM The addition of hydrocyanic acid onto an olefinic double bond in the presence of a catalyst system according to the present invention, in particular the addition onto butadiene or onto 3-pentenitrile, 4-pentenitrile or a mixture of such pentenenitriles or the isomerization of organic nitriles in the presence of a catalyst system according to the present invention, in particular the isomerization of 2-methyl-3-butenitrile to 3-pentenitrile, can advantageously be carried out in the presence of one or more Lewis acids as promoters which influence the activity, selectivity or both of the catalyst system of the present invention. Possible promoters are inorganic and organic compounds in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples which may be mentioned are ZnBr.sub.2, ZnI.sub.2, ZnCl.sub.2, ZnSO.sub.4, CuCl.sub.2, CuCl, Cu(O.sub.3SCF.sub.3).sub.2, CoCl.sub.2, FeI.sub.2, FeCl.sub.3, FeCl.sub.2, FeCl.sub.2(THF).sub.2, TiCl.sub.4(THF).sub.2, TiCl.sub.4, TiCl.sub.3, ClTi(O-iso-Pr).sub.3, MnCl.sub.2, ScCl.sub.3, AlCl.sub.3, (C.sub.8H.sub.17)AlCl.sub.2, (C.sub.8H.sub.17).sub.2AlCl, (iso-C.sub.4H.sub.9).sub.2AlCl, Ph.sub.2AlCl, PhAlCl.sub.2, ReCl.sub.5, ZrCl.sub.4, ZrCl.sub.2, NbCl.sub.5, VCl.sub.3, CrCl.sub.2, MoCl.sub.5, YCl.sub.3, CdCl.sub.2, LaCl.sub.3, Er(O.sub.3SCF.sub.3).sub.3, Yb(O.sub.2CCF.sub.3).sub.3, SmCl.sub.3, B(C.sub.6H.sub.5).sub.3, TaCl.sub.5, as are generally described, for example in U.S. Pat. No. 6,171,996 B1. Further suitable promoters are described in the patents U.S. Pat. No. 3,496,217, U.S. Pat. No. 3,496,218 and U.S. Pat. No. 4,774,353. These comprise metal salts such as ZnCl.sub.2, CoI.sub.2 and SnCl.sub.2, and organometallic compounds such as RAlCl.sub.2, R.sub.3SnO.sub.3SCF.sub.3 and R.sub.3B, where R is an alkyl group or aryl group. U.S. Pat. No. 4,874,884 describes the selection of synergistically effective combinations of promoters to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3 and (C.sub.6H.sub.5).sub.3SnZ, where Z is CF.sub.3SO.sub.3, CH.sub.3C.sub.6H.sub.4SO.sub.3 or (C.sub.6H.sub.5).sub.3BCN.

SUMM The molar ratio of promoter to nickel in the catalyst system can be in the range from 1:16 to 50:1.

SUMM A further advantageous embodiment of hydrocyanation and isomerization may be found in U.S. Pat. No. 5,981,772, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

SUMM A further advantageous embodiment of hydrocyanation may be found in U.S. Pat. No. 6,127,567, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

SUMM A further advantageous embodiment of hydrocyanation and isomerization may be found in U.S. Pat. No. 5,693,843, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

SUMM A further advantageous embodiment of hydrocyanation may be found in U.S. Pat. No. 5,523,453, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

DETD All examples were carried out under a protective argon atmosphere.

DETD 1 equivalent of nickel(0)-(m/p-tolyl phosphite) was admixed with 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 94 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes, 60 minutes and 150 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

Time	MGN	ADN	ADN selectivity (%)
30 min	3.35	10.75	76.2
60 min	6.87	26.39	79.3
150 min	7.11	27.82	79.6

DETD 1 equivalent of Ni(COD).sub.2 was admixed with 3 equivalents of ligand 2 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 142 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and after 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

Time	MGN	ADN	ADN selectivity (%)
30 min	1.80	18.91	91.3
60 min	2.51	32.57	92.9

DETD 1 equivalent of Ni(COD).sub.2 was admixed with 3 equivalents of ligand 1 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 85 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 45 minutes and 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were

obtained:

	Time	MGN	ADN	ADN selectivity (%)
	45 min	1.46	14.12	90.6
	60 min	1.92	21.60	91.8
DETD	1 equivalent of Ni(COD).sub.2 was admixed with 3 equivalents of ligand 3 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 128 equivalents of HCN/h*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and after 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:			

	Time	MGN	ADN	ADN selectivity (%)
	30 min	1.92	24.03	94.5
	60 min	1.93	38.05	95.2
DETD	1 equivalent of Ni(COD).sub.2 was admixed with 3 equivalents of ligand 4 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 106 equivalents of HCN/h*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:			

	Time	MGN	ADN	ADN selectivity (%)
	30 min	1.32	16.61	92.6
	60 min	2.20	36.17	94.3
DETD	1 equivalent of Ni(COD).sub.2 was admixed with 3 equivalents of ligand 6 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 123 equivalents of HCN/h*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:			

	Time	MGN	ADN	ADN selectivity (%)
	30 min	2.24	24.17	91.5
	60 min	3.57	46.91	92.9
DETD	1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was admixed with 3 equivalents of ligand 6 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a			

further 5 minutes. 127 equivalents of HCN/h\*Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

	Time	MGN	ADN	ADN selectivity (%)
	30 min	1.66	20.93	92.6
	60 min	2.74	32.36	92.2
DETD	Virtually no temperature increase occurs. This means that the catalyst is not very active.			
DETD	Virtually no temperature increase occurs. This means that the catalyst is not very active.			
	1. A phosphonite I of the formula 1 or 2 ##STR4## where R1, R2, R5, R6, R7, R8, R9 are each, independently of one another, hydrogen, an alkyl or alkylene group having from 1 to 8 carbon atoms or an alkoxy group having from 1 to 8 carbon atoms, R3 is H or methyl, R4 is i-propyl or t-butyl, X is F, Cl or CF.sub.3 n is 1 or 2 and also methods of preparing them, their use as ligands in transition metal complexes, novel transition metal complexes, processes for preparing them, their use as catalysts and processes carried out in the presence of such transition metal complexes as catalysts.			
	7. The use of a transition metal complex as claimed in claim 4 or 5 as catalyst.			
	8. The use as claimed in claim 7 as catalyst for the addition of hydrocyanic acid onto an olefinic double bond.			
	9. The use as claimed in claim 7 as catalyst for the isomerization of organic nitriles.			
	10. A process for the addition of hydrocyanic acid onto an olefinic double bond in the presence of a transition metal complex as claimed in claim 4 or 5 as catalyst.			
	12. A process for the isomerization of organic nitrites in the presence of a transition metal complex as claimed in claim 4 or 5 as catalyst.			
IT	106-99-0,	1,3-Butadiene, reactions (hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)		
IT	4635-87-4P,	3-Pentenitrile (hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)		
IT	592-51-8P,	4-Pentenitrile 16539-66-1P, trans-3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile 20068-02-4P, cis-2-Methyl-2-butenitrile 26294-98-4P, trans-2-Pentenitrile 28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenitrile (use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)		
IT	74-90-8,	Hydrogen cyanide, reactions (use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)		
IT	106-99-0,	1,3-Butadiene, reactions (hydrocyanation; use of phosphonites as cocatalysts in nickel complex		

10/586490

catalyzed production of nitriles)  
RN 106-99-0 USPATFULL  
CN 1,3-Butadiene (CA INDEX NAME)

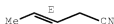


IT 4635-87-4P, 3-Pentenitrile  
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex  
catalyzed production of nitriles)  
RN 4635-87-4 USPATFULL  
CN 3-Pentenitrile (CA INDEX NAME)



IT 16529-66-1P, trans-3-Pentenitrile 16545-78-1P,  
cis-3-Pentenitrile  
(use of phosphonites as cocatalysts in nickel complex catalyzed production  
of nitriles)  
RN 16529-66-1 USPATFULL  
CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 USPATFULL  
CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions  
(use of phosphonites as cocatalysts in nickel complex catalyzed production  
of nitriles)  
RN 74-90-8 USPATFULL  
CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 43 OF 60 USPATFULL ON STN

ACCESSION . . .

and an organic compound comprising at least one ethylenic unsaturation. This reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the. . .

AB . . . and an organic compound comprising at least one ethylenic unsaturation. This reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the. . .

SUMM [0006] These reactions are generally carried out in the liquid phase in the presence of a catalyst based on a metal, generally nickel, present in the form of a complex with an organic ligand. This reaction can be carried out in a homogeneous medium, the catalyst being soluble in the hydrocyanation medium, in particular in the olefin or the nitrites or in a third solvent. It can also be carried out with a medium exhibiting several liquid phases, the catalyst being soluble in one of the phases, more specifically in the phase formed by a polar third solvent, generally water,. . . the nitrites, at least at ambient temperature. The latter embodiment makes it possible to more easily extract and recover the catalyst and thus to obtain nitrile compounds comprising fewer impurities contributed by the catalyst.

SUMM [0007] These catalytic systems have been disclosed in numerous patents and several classes of ligands have been studied. The ligands are generally organophosphorus. . .

SUMM . . . No. 3,496,217, which discloses the synthesis of adiponitrile by reaction of hydrogen cyanide with butadiene in the presence of a catalyst based on nickel complexed with a ligand, such as triaryl phosphite. This reaction is carried out with catalysis in a single-phase medium.

SUMM . . . for the synthesis of adiponitrile by hydrocyanation of butadiene. The reaction is carried out in a two-phase liquid medium, the catalyst being present in an aqueous phase. This process makes it possible to recover the adiponitrile, devoid of catalyst and therefore of metal, in the organic phase. The catalyst disclosed is also a catalyst based on a metal, such as nickel, in combination with a ligand of the phosphine type. However, this ligand comprises sulphonate radicals, making it possible to render the catalyst soluble or dispersible in water.

SUMM [0010] Furthermore, it is also known to combine the nickel-based catalyst with promoters, such as Lewis acids, such as, for example, zinc chloride or triphenylborane, for the hydrocyanation of an unsaturated. . .

SUMM . . . Research is continually being undertaken to improve the performance of the synthesis of nitrites by hydrocyanation, either by developing novel catalytic systems or by modifying the reaction conditions and compositions of the hydrocyanation medium.

SUMM . . . makes it possible to obtain high yields of and high selectivities for linear nitrites and an improved stability of the catalytic system.

SUMM [0015] According to one characteristic of the invention, the reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the. . .

SUMM . . . miscible at the reaction temperature. The reaction is carried out in a nonhomogeneous or two-phase medium. In this embodiment, the catalytic system is advantageously soluble in the ionic liquid.

SUMM . . . of the hydrocyanated products and of the ionic liquid, in particular in order to make possible the extraction of the catalytic system. This is because the solvent of low polarity has the role of rendering the ionic liquid insoluble in the. . .

SUMM [0019] Whatever the embodiment, it is preferable for the catalytic system to be at least partially miscible in the ionic liquid. Advantageously, this miscibility can be obtained by the presence. . .

SUMM [0020] The catalytic systems suitable for the invention are those which preferably comprise the element nickel in the zero oxidation state or a. . . or more generally compounds comprising phosphorus capable of giving a coordination compound with transition metals and more particularly the abovementioned catalytic metals, in particular with nickel. These compounds can be mono-, bi- or polydentate and can exhibit a hydrophobic or hydrophilic. . .

SUMM [0021] Such catalytic systems and their preparation processes are disclosed, for example, in French Patents 2 338 253, 2 710 909, 2 711. . .

SUMM [0025] As is disclosed in the above-mentioned patents, the catalyst can be prepared before its introduction into the medium or in situ.

SUMM [0026] For this, use is preferably made of the compounds of the metals forming the catalytic element, such as nickel, which are added to a medium in which the organophosphorus ligand is also soluble. Such a medium can be the ionic liquid. The catalytic system thus formed is added to the hydrocyanation medium.

SUMM . . . at a temperature of less than 100° C. are preferred as they make possible better separation and extraction of the catalyst from the reaction medium in the case of a two-phase system.

SUMM [0047] The amount of ligand used to form the catalyst is chosen so that the number of moles of this compound with respect to 1 mol of transition metal is. . .

SUMM . . . batchwise implementation, it is in practice possible to charge to a reactor, purged beforehand using an inert gas (such as nitrogen or argon), either a solution comprising all or a portion of the various constituents, the transition metal compound, the possible reducing agents. . .

SUMM . . . mixture is withdrawn after cooling and the reaction products are isolated, for example by separation of the phase comprising the catalytic system and of the phase formed by the solvent of low or no polarity, the hydrocyanated products and those which. . .

SUMM . . . product to be hydrocyanated is an unsaturated compound comprising a nitrile functional group, it is advantageous to use, with the catalytic system, a cocatalyst comprising at least one Lewis acid.

SUMM . . . of linear dinitriles with respect to all the dinitriles formed, and/or to increase the activity and the lifetime of the catalyst.

SUMM [0071] In the context of this preferred alternative form, the catalytic system being already present for the reaction for the hydrocyanation of butadiene, it is sufficient to halt any introduction of. . .

SUMM . . . it is possible, if appropriate, to carry out a slight flushing of the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.

SUMM [0075] As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic system used for the isomerization can be prepared before its introduction into the reaction region. It is also possible to prepare the catalytic system "in situ" by simple mixing of these various constituents. The amount of transition metal compound and more particularly of. . .

SUMM . . . unsaturated nitrites to dinitriles to be carried out with a reaction system in accordance with the invention or any other



- catalytic system already known for this reaction.
- DETD . . . 300 ml of distilled water. 61.62 g (0.215 mol) of lithium bis(trifluoromethylsulfonyl)amide are added and the mixture is stirred under argon for 72 hours at ambient temperature. A two-phase system is formed. After extraction with 250 ml of dichloromethane, the organic. .
- DETD . . . 300 ml of distilled water. 69.46 g (0.242 mol) of lithium bis(trifluoromethylsulfonyl)amide are added and the mixture is stirred under argon for 72 hours at ambient temperature. A two-phase system is formed. After extraction with 250 ml of dichloromethane, the organic. .
- DETD . . . g (0.199 mol) of 1-butyl-2,3-dimethylimidazolium chloride are dissolved in 150 ml of acetone. After vigorous stirring at ambient temperature under argon for 72 hours, the solution is filtered through celite and then concentrated. After chromatography on an alumina column (eluent: dichloromethane),. . .
- DETD [0110] The following are introduced successively and under argon into a glass tube:
- DETD . . . 100° C. for 3 hours with head cooling. At the end of the reaction, the tubes are cooled in liquid nitrogen. A known amount of butylbenzene (approximately 40 mg, to act as chromatography internal standard) is added to the two-phase reaction. . .
- DETD . . . with various salts are collated in Table II below. By way of comparison, a test was carried out with a catalyst based on nickel and on a ligand, triphenylphosphine, in a single-phase medium.

TABLE II

	DC (%)	YD (%)	YD. . .	Mass
DETD	[0120] The following are introduced successively and under argon into a glass tube:			
CLM	What is claimed is:			
. . .	by reaction between hydrogen cyanide and an organic compound having at least one ethylenic unsaturation in the presence of a catalyst comprising an element selected from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, said process comprising. . .			
	40. The process according to claim 26, wherein the metal element of the catalyst is nickel in the 0 or 1 oxidation state.			
IT 106-99-0,	1,3-Butadiene, reactions			
	(hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)			
IT 592-51-8P,	4-Pentenitrile 4635-87-4P, 3-Pentenitrile			
manufacture	(isomerization product and hydrocyanation substrate; process for of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)			
IT 74-90-8,	Hydrogen cyanide, reactions			
	(process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)			
PI US 2004260112	A1 20041223			--
AB	The present invention relates to the manufacture of nitrile compounds from unsaturated organic compounds by reaction with hydrogen cyanide. It relates more particularly to the manufacture of nitrile compounds of use in the synthesis of adiponitrile, an important chemical intermediate in the manufacture of major chemical compounds, such as hexamethylenediamine and $\epsilon$ -caprolactam. The invention provides a process for the manufacture of organic compounds comprising at least one nitrile functional group by carrying out a			

hydrocyanation reaction between hydrogen cyanide and an organic compound comprising at least one ethylenic unsaturation. This reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the reaction medium additionally comprising an ionic liquid in the liquid state at least at the temperature at which the hydrocyanation reaction is carried out.]

SUMM [0006] These reactions are generally carried out in the liquid phase in the presence of a catalyst based on a metal, generally nickel, present in the form of a complex with an organic ligand. This reaction can be carried out in a homogeneous medium, the catalyst being soluble in the hydrocyanation medium, in particular in the olefin or the nitrites or in a third solvent. It can also be carried out with a medium exhibiting several liquid phases, the catalyst being soluble in one of the phases, more specifically in the phase formed by a polar third solvent, generally water, which phase is distinct from that formed by the olefin and the nitrites, at least at ambient temperature. The latter embodiment makes it possible to more easily extract and recover the catalyst and thus to obtain nitrile compounds comprising fewer impurities contributed by the catalyst.

SUMM [0007] These catalytic systems have been disclosed in numerous patents and several classes of ligands have been studied. The ligands are generally organophosphorus compounds, such as phosphites, phosphinites, phosphonites or phosphines. They can be monodentate or polydentate. In the case of processes in a two-phase medium, these organophosphorus ligands advantageously comprise one or more ionizable groups, such as sulphonate, phosphonate, carboxylate or ammonium groups, for example, to render them soluble in the polar phase.

SUMM [0008] Mention may be made, as example of the disclosure of these processes, of U.S. Pat. No. 3,496,217, which discloses the synthesis of adiponitrile by reaction of hydrogen cyanide with butadiene in the presence of a catalyst based on nickel complexed with a ligand, such as triaryl phosphite. This reaction is carried out with catalysis in a single-phase medium.

SUMM [0009] With regard to French Patent No. 2 338 253, it also discloses a process for the synthesis of adiponitrile by hydrocyanation of butadiene. The reaction is carried out in a two-phase liquid medium, the catalyst being present in an aqueous phase. This process makes it possible to recover the adiponitrile, devoid of catalyst and therefore of metal, in the organic phase. The catalyst disclosed is also a catalyst based on a metal, such as nickel, in combination with a ligand of the phosphine type. However, this ligand comprises sulphonate radicals, making it possible to render the catalyst soluble or dispersible in water.

SUMM [0010] Furthermore, it is also known to combine the nickel-based catalyst with promoters, such as Lewis acids, such as, for example, zinc chloride or triphenylborane, for the hydrocyanation of an unsaturated nitrile compound.

SUMM [0011] Research is continually being undertaken to improve the performance of the synthesis of nitrites by hydrocyanation, either by developing novel catalytic systems or by modifying the reaction conditions and compositions of the hydrocyanation medium.

SUMM [0013] One of the aims of the present invention is to provide a novel process for the manufacture of nitrites by hydrocyanation of an olefin

by reaction with hydrogen cyanide which makes it possible to obtain high yields of and high selectivities for linear nitrites and an improved stability of the catalytic system.

SUMM [0015] According to one characteristic of the invention, the reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the reaction medium additionally comprising an ionic liquid which is in the liquid state at least at the temperature at which the hydrocyanation reaction is carried out.

SUMM [0017] In a second embodiment, the ionic liquid and the compound to be hydrocyanated are immiscible or are only partially miscible at the reaction temperature. The reaction is carried out in a nonhomogeneous or two-phase medium. In this embodiment, the catalytic system is advantageously soluble in the ionic liquid.

SUMM [0018] In both these embodiments, it is possible to add a solvent of low polarity. This solvent of low polarity can be added from the beginning of the reaction but can also be used only after the end of the reaction, in order thus to promote the separation of the hydrocyanated products and of the ionic liquid, in particular in order to make possible the extraction of the catalytic system. This is because the solvent of low polarity has the role of rendering the ionic liquid insoluble in the phase composed of the said solvent, the unconverted olefin and the nitrile compounds formed.

SUMM [0019] Whatever the embodiment, it is preferable for the catalytic system to be at least partially miscible in the ionic liquid. Advantageously, this miscibility can be obtained by the presence of at least one ionizable group in the molecule of the organophosphorus ligand. Mention may be made, as ionizable groups, of groups of anionic type, such as sulphonate, phosphonate, phosphinate, carboxylate or sulphinate, or of cationic type, such as guanidinium, ammonium, pyridinium, imidazolium, phosphonium or sulphonium, for example. The number and the nature of these ionic groups are preferably chosen in order to render the ligand soluble in the ionic liquid. It can be advantageous for the nature of the ionizable group to be identical to that of the anion or of the cation associated with the ionic liquid.

SUMM [0020] The catalytic systems suitable for the invention are those which preferably comprise the element nickel in the zero oxidation state or a complex with organophosphorus ligands which can comprise several ionizable groups described above or more generally compounds comprising phosphorus capable of giving a coordination compound with transition metals and more particularly the abovementioned catalytic metals, in particular with nickel. These compounds can be mono-, bi- or polydentate and can exhibit a hydrophobic or hydrophilic nature. These compounds have been disclosed in numerous patents relating to the hydrocyanation of butadiene and belong to several classes, including in particular the organophosphonates, organophosphonites, organophosphinites and organophosphines.

SUMM [0021] Such catalytic systems and their preparation processes are disclosed, for example, in French Patents 2 338 253, 2 710 909, 2 711 987, 2 739 378 and 2 778 915.

SUMM [0025] As is disclosed in the above-mentioned patents, the catalyst can be prepared before its introduction into the medium or in situ.

- SUMM [0026] For this, use is preferably made of the compounds of the metals forming the catalytic element, such as nickel, which are added to a medium in which the organophosphorus ligand is also soluble. Such a medium can be the ionic liquid. The catalytic system thus formed is added to the hydrocyanation medium.
- SUMM [0042] The ionic liquid, to be suitable for the process of the invention, must be in the liquid state at least at the temperature at which the hydrocyanation reaction is carried out. However, ionic liquids which are found in the liquid state at a temperature of less than 100° C. are preferred as they make possible better separation and extraction of the catalyst from the reaction medium in the case of a two-phase system.
- SUMM [0047] The amount of ligand used to form the catalyst is chosen so that the number of moles of this compound with respect to 1 mol of transition metal is between 0.5 and 50 and preferably between 2 and 10.
- SUMM [0052] In the context of a batchwise implementation, it is in practice possible to charge to a reactor, purged beforehand using an inert gas (such as nitrogen or argon), either a solution comprising all or a portion of the various constituents, the transition metal compound, the possible reducing agents and solvents, or the said constituents separately. Generally, the reactor is then brought to the chosen temperature and then the compound to be hydrocyanated is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and unvaryingly.
- SUMM [0053] When the reaction is complete, the reaction mixture is withdrawn after cooling and the reaction products are isolated, for example by separation of the phase comprising the catalytic system and of the phase formed by the solvent of low or no polarity, the hydrocyanated products and those which have not been converted, in the case of a two-phase system. The products from the latter phase can be separated, for example by distillation. In the case of a single-phase system, other separation means can be employed, such as, for example, distillation or liquid/liquid extraction.
- SUMM [0054] In the case where the product to be hydrocyanated is an unsaturated compound comprising a nitrile functional group, it is advantageous to use, with the catalytic system, a cocatalyst comprising at least one Lewis acid.
- SUMM [0057] The Lewis acid used as cocatalyst makes it possible in particular, in the case of the hydrocyanation of aliphatic nitriles comprising ethylenic unsaturation, to improve the linearity of the dinitriles obtained, that is to say the percentage of linear dinitriles with respect to all the dinitriles formed, and/or to increase the activity and the lifetime of the catalyst.
- SUMM [0071] In the context of this preferred alternative form, the catalytic system being already present for the reaction for the hydrocyanation of butadiene, it is sufficient to halt any introduction of hydrogen cyanide to allow the isomerization reaction to take place.
- SUMM [0072] In this alternative form, it is possible, if appropriate, to carry out a slight flushing of the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.

- SUMM [0075] As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic system used for the isomerization can be prepared before its introduction into the reaction region. It is also possible to prepare the catalytic system "in situ" by simple mixing of these various constituents. The amount of transition metal compound and more particularly of nickel compound used and the amount of ligand are the same as for the hydrocyanation reaction.
- SUMM [0076] However, the preparation of dinitrile compounds by hydrocyanation of an olefin such as butadiene can be carried out using a reaction system in accordance with the invention for the stages of formation of the unsaturated nitrites and the stage of isomerization above, it being possible for the reaction for the hydrocyanation of the unsaturated nitrites to dinitriles to be carried out with a reaction system in accordance with the invention or any other catalytic system already known for this reaction.
- DETD [0081] 40.50 g (0.215 mol) of 1-butyl-2,3-dimethylimidazolium chloride are dissolved in 300 ml of distilled water. 61.62 g (0.215 mol) of lithium bis(trifluoromethylsulphonyl)amide are added and the mixture is stirred under argon for 72 hours at ambient temperature. A two-phase system is formed. After extraction with 250 ml of dichloromethane, the organic phase is washed with 800 ml of water and then concentrated. The compound exists in the form of a slightly pinkish liquid which is purified by chromatography on a neutral alumina column (eluent: dichloromethane). It is then concentrated, taken up in acetonitrile in the presence of active carbon and filtered. After drying for several hours at 60° C., the compound is obtained in the form of a colourless liquid (83.78 g, 90%). The structure of this product: C.sub.11H.sub.17N.sub.3S.sub.2O.sub.4F.sub.6, is confirmed by NMR spectral analysis.
- DETD [0083] 41.92 g (0.240 mol) of 1-butyl-3-methylimidazolium chloride are dissolved in 300 ml of distilled water. 69.46 g (0.242 mol) of lithium bis(trifluoromethylsulphonyl)amide are added and the mixture is stirred under argon for 90 hours at ambient temperature. A two-phase system is formed. After extraction with 250 ml of dichloromethane, the organic phase is washed with 800 ml of water and then concentrated. The compound exists in the form of a slightly pinkish liquid which is purified by chromatography on a neutral alumina column (eluent: dichloromethane). It is then concentrated, taken up in acetonitrile in the presence of active carbon and filtered. After drying for several hours at 60° C., the compound is obtained in the form of a colourless liquid (81.47 g). Its structure, C.sub.10H.sub.15N.sub.3S.sub.2O.sub.4F.sub.6, was confirmed by NMR analysis.
- DETD [0085] 33.37 g (0.200 mol) of sodium hexafluorophosphate and 37.50 g (0.199 mol) of 1-butyl-2,3-dimethylimidazolium chloride are dissolved in 150 ml of acetone. After vigorous stirring at ambient temperature under argon for 72 hours, the solution is filtered through celite and then concentrated. After chromatography on an alumina column (eluent: dichloromethane), the salt is taken up in acetonitrile in the presence of active carbon and filtered. Concentrating the solution gives 50.41 g (0.170 mol, 85%) of a white solid. The structure of this product, C.sub.9H.sub.17N.sub.2PF.sub.6, is confirmed by NMR spectral analysis.
- DETD [0110] The following are introduced successively and under argon into a glass tube:
- DETD [0115] The tube is closed, then stirred and heated at 100° C. for 3 hours with head cooling. At the end of the reaction, the tubes are cooled in liquid nitrogen. A known amount of butylbenzene (approximately 40 mg, to act as chromatography internal standard) is

added to the two-phase reaction medium, which is diluted and homogenized by the addition of 10 ml of THF. The solution obtained is filtered through a short silica column and injected in gas chromatography (GC). [0117] The results obtained with various salts are collated in Table II below. By way of comparison, a test was carried out with a catalyst based on nickel and on a ligand, triphenylphosphine, in a single-phase medium.

TABLE II

Ex. Salt	DC (%)		YD (%)		Mass balance (%)
	2M3BN	3PN + 4PN	2M2BN	2PN	
A (1)	42	57	-3.1	5.8	86
1 [BMI] [TF.sub.2N]	95	90	2.9	-0.4	96
2 [BMMI] [PF.sub.6]	93	90	0.2	2.3	94
3 [BMMI] [TF.sub.2N]	96	94	0.8	1.6	98

(1) comparative test without ionic liquid with triphenylphosphine as ligand  
DETD [0120] The following are introduced successively and under argon into a glass tube:

26. A process for the manufacture of organic compounds comprising at least one nitrile functional group by reaction between hydrogen cyanide and an organic compound having at least one ethylenic unsaturation in the presence of a catalyst comprising an element selected from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, said process comprising the step of carrying out said reaction in a reaction medium with the presence of an ionic liquid which comprises at least one cation and at least one anion and which is liquid at least at a temperature at which the reaction is carried out.

40. The process according to claim 26, wherein the metal element of the catalyst is nickel in the 0 or 1 oxidation state.

IT 106-99-0, 1,3-Butadiene, reactions

(hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 592-51-8P, 4-Pentenitrile 4635-87-4F, 3-Pentenitrile

(isomerization product and hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 74-90-8, Hydrogen cyanide, reactions

(process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 106-99-0, 1,3-Butadiene, reactions

(hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



10/586490

IT 4635-87-4P, 3-Pentenitrile  
 (isomerization product and hydrocyanation substrate; process for  
 manufacture  
 of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid  
 solvents)  
 RN 4635-87-4 USPATFULL  
 CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions  
 (process for manufacture of nitriles by hydrocyanation of unsatd. compds.  
 with HCN in ionic liquid solvents)  
 RN 74-90-8 USPATFULL  
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 44 OF 60 USPATFULL on STN  
 ACCESSION NUMBER: 2004:228236 USPATFULL Full-text  
 TITLE: Catalyst system containing ni(0) for hydrocyanation  
 INVENTOR(S): Bartsch, Michael, Neustadt, GERMANY, FEDERAL REPUBLIC  
 OF  
 Baumann, Robert, Mannheim, GERMANY, FEDERAL REPUBLIC OF  
 Kunsmann-Keitel, Dagmar Pascale, Limburgerhof,  
 GERMANY, FEDERAL REPUBLIC OF  
 Haderlein, Gerd, Darmstadt, GERMANY, FEDERAL REPUBLIC  
 OF  
 Jungkamp, Tim, Dossenheim, GERMANY, FEDERAL REPUBLIC OF  
 Altmayer, Marco, Mannheim, GERMANY, FEDERAL REPUBLIC OF  
 Seigel, Wolfgang, Limburgerhof, GERMANY, FEDERAL  
 REPUBLIC OF

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2004176622	A1	20040909	<--
APPLICATION INFO.:	US 2004-484169	A1	20040120	(10)
	WO 2002-EP7888		20020716	

	NUMBER	DATE
PRIORITY INFORMATION:	DE 2001-10136488	20010727
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	KEIL & WEINKAUF, 1350 CONNECTICUT AVENUE, N.W., WASHINGTON, DC, 20036	
NUMBER OF CLAIMS:	21	
EXEMPLARY CLAIM:	1	
LINE COUNT:	1060	

## CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A catalyst system containing a) Ni (0), b) 4-10 mol per mol Ni (0) according to a) a compound (I) of formula P (X.sup.1R.sup.1) (X.sup.2R.sup.2) (X.sup.3R.sup.3) (I) wherein X.sup.1, X.sup.2, X.sup.3 independently represent oxygen or a single bond R.sup.1, R.sup.2, R.sup.3 represent independently, the same or different organic radicals, and c) 1-4 mol per mol Ni (0) according to a) a compound (II) of formula (II) wherein X.sup.11, X.sup.12, X.sup.13, X.sup.21, X.sup.22, X.sup.23 independently oxygen or a single bond, R.sup.11, R.sup.12 independently represent the same or different individual or bridged organic radicals, R.sup.21, R.sup.22 independently represent the same or different, individual or bridged organic radicals, Y represents a bridge group. The invention also relates to a method for the production of mixtures of monoolefin C.sub.5-mono nitriles with a n-conjugated C.dbd.C and C.dbd.N bond by hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene in the presence of at least one such system and to a method for the production of a dinitrile by hydrocyanation of a mixture of monoolefin C.sub.5-mono nitriles with a non-conjugated C.dbd.C-- and C.dbd.N bond in the presence of at least one such system. ##STR1##

## CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Catalyst system containing ni(0) for hydrocyanation

AB A catalyst system containing a) Ni (0), b) 4-10 mol per mol Ni (0) according to a) a compound (I) of formula. . .

SUMM [0015] which is suitable as catalyst and to processes for preparing such systems.

SUMM [0016] Systems comprising Ni(0) and a compound (II) which are suitable as catalysts for the hydrocyanation of butadiene to form a mixture of isomeric pentenenitriles and of pentenenitrile to form adiponitrile and processes. . .

SUMM [0017] The preparation of these catalyst systems is technically complicated and expensive. This applies particularly since the catalyst systems are gradually decomposed during use and thus have to be discharged and replaced by fresh catalyst.

SUMM . . . nickel as Ni(0) source with compound (II) in the presence or absence of a liquid diluent or hydrogen halide as catalyst leads to a large extent to decomposition of compound (II).

SUMM . . . chloride and zinc as Ni(0) source is known. A disadvantage of this process is the simultaneous formation of the specified catalyst system and zinc chloride.

SUMM [0022] If the use of the pure catalyst system is envisaged, the zinc chloride firstly has to be removed before use, which is costly.

SUMM [0023] If the mixture of catalyst system and zinc chloride is used instead of the pure catalyst system, then the work-up of the mixture of exhausted catalyst system and zinc chloride poses a great problem.

SUMM [0024] A further disadvantage of the catalyst system comprising Ni(0) and compound (II) is that compound (II) can be obtained only by way of a technically complicated. . .

SUMM [0025] It is an object of the present invention to provide a catalyst system which can be synthesized in a technically simple and economical way and displays selectivities and activities comparable to those of a catalyst system comprising Ni(0) and compound (II), especially in the hydrocyanation of compounds having conjugated olefinic double bonds, e.g. butadiene, and. . .

SUMM . . . first system in step a) can advantageously be carried out in the presence of a homogeneous or heterogeneous, preferably homogeneous, catalyst.

SUMM [0092] As homogeneous catalyst, it is advantageous to use a protic acid or a mixture of such protic acids, for example hydrochloric acid.

SUMM [0093] An advantageous homogeneous catalyst is a compound of the formula



- SUMM [0095] The catalyst used in step a) can be carried over from step a) to step b). It has been found to be advantageous to remove the catalyst from step a) between steps a) and b).
- SUMM . . . monoolefinic C.sub.5-mono nitriles having nonconjugated C.dbd.C and C.dbd.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the above-described systems according to the present invention.
- SUMM . . . which a C.dbd.C double bond is conjugated with the C.dbd.N bond may be obtained. It is known from "Applied Homogeneous Catalysis with Organometallic Compounds", vol. 1, V. C. H. Weinheim, p. 479, that the conjugated 2-pentenitrile formed in the isomerization of. . . has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an untreated C.sub.4 fraction also act as catalyst poisons for the first reaction step of the production of adipic acid, viz. the monoaddition of hydrogen cyanide.
- SUMM [0105] For this reason, those components which act as catalyst poisons in catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof, are advantageously removed completely or partially from the hydrocarbon mixture. To remove these components, the C.sub.4 fraction is subjected to a catalytic partial hydrogenation prior to the addition of hydrogen cyanide. This partial hydrogenation is carried out in the presence of a hydrogenation catalyst which is capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.
- SUMM [0106] Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the oxides, in particular silicon and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., customary for this purpose and mixtures thereof. Preferred supports are Al.sub.2O.sub.3, SiO.sub.2 and mixtures thereof. In particular, the heterogeneous catalysts used are those described in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on Cu are marketed by Dow Chemical as KLP catalyst.
- SUMM [0111] a) charging a reactor with the hydrocarbon mixture, if desired part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired one produced in situ, and, if desired, a solvent,
- SUMM [0116] The pressure-rated reactor is charged with the partially hydrogenated C.sub.4 fraction, hydrogen cyanide, a hydrocyanation catalyst and, if desired, a solvent prior to commencement of the reaction. Suitable solvents are those mentioned above for the preparation of the catalysts of the present invention, preferably aromatic hydrocarbons such as toluene and xylene or tetrahydrofuran.
- SUMM . . . working up the remaining reaction mixture by distillation to separate off the desired product and to recover the still active catalyst.
- SUMM . . . high proportion of 3-pentenitrile or 4-pentenitrile and a very low proportion of conjugated 2-pentenitrile and 2-methyl-2-butenitrile, which may act as catalyst poisons, should be formed.
- SUMM [0126] Advantageously, the catalysts of the present invention based on phosphonite ligands are also suitable for the structural isomerization and double bond isomerization in. . .
- SUMM [0128] Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation. . . cyanide in the hydrocyanation without appreciable precipitation of inactive nickel(II) compounds, e.g. nickel(II) cyanide, occurring. In contrast to known hydrocyanation catalysts based on uncomplexed phosphine and phosphite

ligands, the catalysts of the formula I are thus suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide. . . also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. Thus, the catalysts used according to the present invention and the hydrocyanation processes based on them generally allow greater recirculation of catalysts and display longer catalyst operating lives than do known processes. This is advantageous both in terms of improved economics and also from an ecological point of view, since the nickel cyanide formed from the active catalyst by reaction with hydrogen cyanide is highly toxic and has to be worked up or disposed of, which is very. . .

SUMM . . . can be derived from U.S. Pat. No. 6,981,772, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

SUMM . . . can be derived from U.S. Pat. No. 6,127,567, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

SUMM . . . can be derived from U.S. Pat. No. 5,693,843, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

SUMM . . . can be derived from U.S. Pat. No. 5,523,453, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

DETD [0136] All examples were carried out under a protective argon atmosphere.

DETD . . . to this mixture and the mixture was stirred for a further 5 minutes. 94 molar equivalents of HCN/hour\*Ni in an argon carrier gas stream were passed in. Samples were taken after 30 minutes, 60 minutes and 150 minutes and the following. . .

DETD . . . to this mixture and the mixture was stirred for a further 5 minutes. 133 molar equivalents of HCN/hour\*Ni in an argon carrier gas stream were passed in.

DETD [0158] The procedure of Example 10 was repeated (using 0.58 mmol of Ni(0)), except that the catalyst mixture was stirred at 25°C. for 12 hours instead of 1 hour and 122 molar equivalents of HCN/h\*Ni were. . .

CLM What is claimed is:

. . . R.sup.1, R.sup.2, R.sup.3 are each, independently of one another, a phenyl, o-tolyl, m-tolyl or p-tolyl group, which is suitable as catalyst.

. . . to 9, wherein the preparation of the first system in step a) is carried out in the presence of a catalyst.

. . . 9, wherein the preparation of the first system in step a) is carried out in the presence of a homogeneous catalyst.

. . . preparation of the first system in step a) is carried out in the presence of a protic acid as homogeneous catalyst.

. . . the preparation of the first system in step a) is carried out in the presence of hydrogen chloride as homogeneous catalyst.

. . . (R.sup.1X.sup.1)(R.sup.2X.sup.2)PCl or (R.sup.1X.sup.1)PCl.sub.2, where X.sup.1, X.sup.2, R.sup.1, R.sup.2 are as defined in any of claims

1 to 8, as homogeneous catalyst.

15. A process as claimed in any of claims 6 to 14, wherein the catalyst is removed between step a) and step b).

- . . . monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.
  - . . . dinitrile by hydrocyanation of a mixture of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.
  - . . . adiponitrile by hydrocyanation of a mixture of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.
- IT 111-69-3P, Adipodinitrile 16529-66-1F, trans-3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile 20068-02-4P, cis-2-Methyl-2-butenitrile 25899-50-7P, cis-2-Pentenitrile 26294-98-4P, trans-2-Pentenitrile 28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenitrile  
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 4635-87-4P, 3-Pentenitrile  
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 74-90-6, Hydrocyanic acid, reactions 106-99-0, 1,3-Butadiene, reactions 16529-56-9, 2-Methyl-3-butenitrile  
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- TI Catalyst system containing ni(0) for hydrocyanation|
- PI US 2004176622 A1 20040909 <--|
- AB A catalyst system containing a) Ni (0), b) 4-10 mol per mol Ni (0) according to a) a compound (I) of formula P (X.sup.1R.sup.1) (X.sup.2R.sup.2) (X.sup.3R.sup.3) (I) wherein X.sup.1, X.sup.2, X.sup.3 independently represent oxygen or a single bond R.sup.1, R.sup.2, R.sup.3 represent independently, the same or different organic radicals, and c) 1-4 mol per mol Ni (0) according to a) a compound (II) of formula (II) wherein X.sup.11, X.sup.12, X.sup.13, X.sup.21, X.sup.22, X.sup.23 independently oxygen or a single bond, R.sup.11, R.sup.12 independently represent the same or different individual or bridged organic radicals, R.sup.21, R.sup.22 independently represent the same or different, individual or bridged organic radicals, Y represents a bridge group. The invention also relates to a method for the production of mixtures of monoolefin C.sub.5-mononitrils with a n-conjugated C.dbd.C and C.dbd.N bond by hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene in the presence of at least one such system and to a method for the production of a dinitrile by hydrocyanation of a mixture of monoolefin C.sub.5-mononitriles with a non-conjugated C.dbd.C-- and C.dbd.N bond in the presence of at least one such system. ##STR1##|
- SUMM [0015] which is suitable as catalyst and to processes for preparing such systems.
- SUMM [0016] Systems comprising Ni(0) and a compound (II) which are suitable as catalysts for the hydrocyanation of butadiene to form a mixture of isomeric pentenenitriles and of pentenenitrile to form adiponitrile and processes for preparing them are known per se, for example from U.S.

Pat. No. 3,903,120, U.S. Pat. No. 5,523,453, U.S. Pat. No. 5,981,772, U.S. Pat. No. 6,127,567, U.S. Pat. No. 5,693,843, U.S. Pat. No. 5,847,191, WO 01/14392.

- SUMM [0017] The preparation of these catalyst systems is technically complicated and expensive. This applies particularly since the catalyst systems are gradually decomposed during use and thus have to be discharged and replaced by fresh catalyst.
- SUMM [0018] The direct reaction of metallic nickel as Ni(0) source with compound (II) in the presence or absence of a liquid diluent or hydrogen halide as catalyst leads to a large extent to decomposition of compound (II).
- SUMM [0021] The preparation of the system comprising Ni(0) and compound (II) starting from nickel chloride and zinc as Ni(0) source is known. A disadvantage of this process is the simultaneous formation of the specified catalyst system and zinc chloride.
- SUMM [0022] If the use of the pure catalyst system is envisaged, the zinc chloride firstly has to be removed before use, which is costly.
- SUMM [0023] If the mixture of catalyst system and zinc chloride is used instead of the pure catalyst system, then the work-up of the mixture of exhausted catalyst system and zinc chloride poses a great problem.
- SUMM [0024] A further disadvantage of the catalyst system comprising Ni(0) and compound (II) is that compound (II) can be obtained only by way of a technically complicated and expensive synthesis.
- SUMM [0025] It is an object of the present invention to provide a catalyst system which can be synthesized in a technically simple and economical way and displays selectivities and activities comparable to those of a catalyst system comprising Ni(0) and compound (II), especially in the hydrocyanation of compounds having conjugated olefinic double bonds, e.g. butadiene, and of compounds having one olefinic double bond and another unsaturated group, e.g. 2-pentenitrile, 3-pentenitrile, 4-pentenitrile, 2-pentenoic esters, 3-pentenoic esters or 4-pentenoic esters.
- SUMM [0091] The preparation of the first system in step a) can advantageously be carried out in the presence of a homogeneous or heterogeneous, preferably homogeneous, catalyst.
- SUMM [0092] As homogeneous catalyst, it is advantageous to use a protic acid or a mixture of such protic acids, for example hydrochloric acid.
- SUMM [0093] An advantageous homogeneous catalyst is a compound of the formula
- SUMM [0095] The catalyst used in step a) can be carried over from step a) to step b). It has been found to be advantageous to remove the catalyst from step a) between steps a) and b).
- SUMM [0099] The present invention further provides a process for preparing mixtures of monoolefinic C.sub.5-monoitriles having nonconjugated C.dbd.C and C.dbd.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the above-described systems according to the present invention.

- SUMM [0104] C.sub.4 fractions are, if appropriate, substantially free of alkynes, e.g. propyne or butyne, of 1,2-dienes, e.g. propadiene, and of alkenynes, e.g. vinylacetylene. Otherwise, products in which a C.dbd.C double bond is conjugated with the C.dbd.N bond may be obtained. It is known from "Applied Homogeneous Catalysis with Organometallic Compounds", vol. 1, V. C. H. Weinheim, p. 479, that the conjugated 2-pentenitrile formed in the isomerization of 2-methyl-3-butenitrile and 3-pentenitrile acts as a reaction inhibitor for the second addition of hydrogen cyanide to form adiponitrile. It has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an untreated C.sub.4 fraction also act as catalyst poisons for the first reaction step of the production of adipic acid, viz. the monoaddition of hydrogen cyanide.
- SUMM [0105] For this reason, those components which act as catalyst poisons in catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof, are advantageously removed completely or partially from the hydrocarbon mixture. To remove these components, the C.sub.4 fraction is subjected to a catalytic partial hydrogenation prior to the addition of hydrogen cyanide. This partial hydrogenation is carried out in the presence of a hydrogenation catalyst which is capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.
- SUMM [0106] Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the oxides, in particular silicon and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., customary for this purpose and mixtures thereof. Preferred supports are Al.sub.2O.sub.3, SiO.sub.2 and mixtures thereof. In particular, the heterogeneous catalysts used are those described in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on Cu are marketed by Dow Chemical as KLP catalyst.
- SUMM [0111] a) charging a reactor with the hydrocarbon mixture, if desired part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired one produced in situ, and, if desired, a solvent,
- SUMM [0116] The pressure-rated reactor is charged with the partially hydrogenated C.sub.4 fraction, hydrogen cyanide, a hydrocyanation catalyst and, if desired, a solvent prior to commencement of the reaction. Suitable solvents are those mentioned above for the preparation of the catalysts of the present invention, preferably aromatic hydrocarbons such as toluene and xylene or tetrahydrofuran.
- SUMM [0120] To complete the conversion, the reaction time can be followed by an after-reaction time of from 0 minutes to about 5 hours, preferably from about 1 hour to 3.5 hours, during which no more hydrogen cyanide is fed into the autoclave. The temperature during this time is kept essentially constant at the level of the reaction temperature previously set. Work-up is carried out by customary methods and comprises separating off the unreacted 1,3-butadiene and the unreacted hydrogen cyanide, e.g. by scrubbing or extraction, and working up the remaining reaction mixture by distillation to separate off the desired product and to recover the still active catalyst.
- SUMM [0124] 2. Isomerization of the 2-methyl-3-butenitrile present in these mixtures to form 3-pentenitrile and isomerization of the

3-pentenitrile formed in this way and that already present in the mixture from step 1 to form various n-pentenitriles. Here, a very high proportion of 3-pentenitrile or 4-pentenitrile and a very low proportion of conjugated 2-pentenitrile and 2-methyl-2-butenitrile, which may act as catalyst poisons, should be formed.

- SUMM [0126] Advantageously, the catalysts of the present invention based on phosphonite ligands are also suitable for the structural isomerization and double bond isomerization in step 2 and/or the second addition of hydrogen cyanide in step 3.
- SUMM [0128] Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures but they can also be admixed with an excess of hydrogen cyanide in the hydrocyanation without appreciable precipitation of inactive nickel(II) compounds, e.g. nickel(II) cyanide, occurring. In contrast to known hydrocyanation catalysts based on uncomplexed phosphine and phosphite ligands, the catalysts of the formula I are thus suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide in the reaction mixture can generally be effectively avoided but also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. Thus, the catalysts used according to the present invention and the hydrocyanation processes based on them generally allow greater recirculation of catalysts and display longer catalyst operating lives than do known processes. This is advantageous both in terms of improved economics and also from an ecological point of view, since the nickel cyanide formed from the active catalyst by reaction with hydrogen cyanide is highly toxic and has to be worked up or disposed of, which is very costly.
- SUMM [0130] A further advantageous embodiment of hydrocyanation and isomerization can be derived from U.S. Pat. No. 6,981,772, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.
- SUMM [0131] A further advantageous embodiment of hydrocyanation and isomerization can be derived from U.S. Pat. No. 6,127,567, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.
- SUMM [0132] A further advantageous embodiment of a hydrocyanation process can be derived from U.S. Pat. No. 5,693,843, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.
- SUMM [0133] A further advantageous embodiment of a hydrocyanation process can be derived from U.S. Pat. No. 5,523,453, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.
- DETD [0136] All examples were carried out under a protective argon atmosphere.
- DETD [0144] 1 molar equivalent of nickel(0)-(m/p-tolyl phosphite) (0.6 mmol of Ni(0)) was admixed with 365 molar equivalents of 3-pentenitrile,

the mixture was stirred at 25° C. for 1 hour and heated to 70° C. 1 molar equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 94 molar equivalents of HCN/hour\*Ni in an argon carrier gas stream were passed in. Samples were taken after 30 minutes, 60 minutes and 150 minutes and the following yields (in percent) were determined:

Time	MGN	ADN	ADN selectivity (%)
30 min	3.35	10.75	76.2
60 min	6.87	26.39	79.3
150 min	7.11	27.82	79.6

DETD [0148] 1 molar equivalent of Ni(COD).sub.2 (0.61 mmol of Ni(0)) was admixed with 1 molar equivalent of ligand 1, 4 molar equivalents of m/p-tolyl phosphite (m:p=2:1) and 365 molar equivalents of 3-pentenitrile, the mixture was stirred at 25° C. for 1 hour and heated to 70° C. 1 molar equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 133 molar equivalents of HCN/hour\*Ni in an argon carrier gas stream were passed in.

DETD [0158] The procedure of Example 10 was repeated (using 0.58 mmol of Ni(0)), except that the catalyst mixture was stirred at 25° C. for 12 hours instead of 1 hour and 122 molar equivalents of HCN/h\*Ni were passed in instead of 43 molar equivalents of HCN/h\*Ni.  
1. A system comprising a) Ni(0) b) from 4 to 10 mol per mol of Ni(0) in a) of a compound (I) of the formula P(X.sup.1R.sup.1)(X.sup.2R.sup.2)(X.sup.3R.sup.3) (I) where X.sup.1, X.sup.2, X.sup.3 are each oxygen, R.sup.1, R.sup.2, R.sup.3 are, independently of one another, and c) from 1 to 4 mol per mol of Ni(0) in a) of a compound (II) of the formula ##STR5## where X.sup.11, X.sup.12, X.sup.13 X.sup.21, X.sup.22, X.sup.23 are each oxygen, R.sup.11, R.sup.12 are identical or different, individual or bridged organic radicals, R.sup.21, R.sup.22 are identical or different, individual or bridged organic radicals, Y is a bridging group and R.sup.1, R.sup.2, R.sup.3 are each, independently of one another, a phenyl, o-tolyl, m-tolyl or p-tolyl group, which is suitable as catalyst.

10. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a catalyst.

11. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a homogeneous catalyst.

12. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a protic acid as homogeneous catalyst.

13. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of hydrogen chloride as homogeneous catalyst.

14. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a compound of the formula (R.sup.1X.sup.1)(R.sup.2X.sup.2)PCl or (R.sup.1X.sup.1)PCl.sub.2, where X.sup.1, X.sup.2, R.sup.1, R.sup.2

are as defined in any of claims 1 to 8, as homogeneous catalyst.

15. A process as claimed in any of claims 6 to 14, wherein the catalyst is removed between step a) and step b).

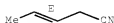
19. A process for preparing mixtures of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.

20. A process for preparing a dinitrile by hydrocyanation of a mixture of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.

21. A process for preparing adiponitrile by hydrocyanation of a mixture of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.

- IT 111-69-3P, Adipodinitrile 16529-66-1E, trans-3-Pentenitrile  
 16545-78-1P, cis-3-Pentenitrile 20068-02-4P,  
 cis-2-Methyl-2-butenitrile 25899-50-7P, cis-2-Pentenitrile  
 26294-98-4P, trans-2-Pentenitrile 28906-50-5P, Methylglutaronitrile  
 30574-97-1P, trans-2-Methyl-2-butenitrile  
 (production of dinitrile monomers from olefinic mononitriles by catalytic  
 isomerization and hydrocyanation)
- IT 4635-97-4P, 3-Pentenitrile  
 (production of dinitrile monomers from olefinic mononitriles by catalytic  
 isomerization and hydrocyanation)
- IT 74-90-6, Hydrocyanic acid, reactions 106-99-0,  
 1,3-Butadiene, reactions 16529-56-9, 2-Methyl-3-butenitrile  
 (production of dinitrile monomers from olefinic mononitriles by catalytic  
 isomerization and hydrocyanation)
- IT 16529-66-1E, trans-3-Pentenitrile 16545-78-1P,  
 cis-3-Pentenitrile  
 (production of dinitrile monomers from olefinic mononitriles by catalytic  
 isomerization and hydrocyanation)
- RN 16529-66-1 USPATFULL  
 CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



- RN 16545-78-1 USPATFULL  
 CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.





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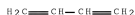
IT 4635-87-4P, 3-Pentenitrile  
(production of dinitrile monomers from olefinic mononitriles by catalytic  
isomerization and hydrocyanation)  
RN 4635-87-4 USPATFULL  
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-99-8, Hydrocyanic acid, reactions 106-99-0,  
1,3-Butadiene, reactions  
(production of dinitrile monomers from olefinic mononitriles by catalytic  
isomerization and hydrocyanation)  
RN 74-99-8 USPATFULL  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL  
CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 45 OF 60 USPATFULL on STN  
ACCESSION NUMBER: 2004:159447 USPATFULL Full-text  
TITLE: Process of synthesis of compounds having nitrile  
functions from ethylenically unsaturated compounds  
INVENTOR(S): Rosier, Cecile, Soucieu En Jarrest, FRANCE  
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PATENT ASSIGNEE(S): RHODIA POLYAMIDE INTERMEDIATES, CEDEX, FRANCE (non-U.S.  
corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 2004122251	A1	20040624
	US 7084293	B2	20060801
APPLICATION INFO.:	US 2003-353912	A1	20030130 (10)

	NUMBER	DATE
PRIORITY INFORMATION:	FR 2002-16550	20021223
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	

LEGAL REPRESENTATIVE: BURNS, DOANE, SWECKER & MATHIS, L.L.P., P.O. Box 1404,  
Alexandria, VA, 22313-1404

NUMBER OF CLAIMS: 27

EXEMPLARY CLAIM: 1

LINE COUNT: 751

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The present invention relates to a process of hydrocyanation of ethylenically unsaturated organic compounds to compounds having at least one nitrile function, particularly the hydrocyanation of diolefins such as butadiene, or of substituted olefins such as alkene nitriles such as pentenenitriles; the subject hydrocyanation is carried out in the presence of a catalytic system comprising a metallic element and mono- and pluri-dentate organophosphorus ligands.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . the context of discontinuous performance, there can be charged into a reactor, purged beforehand with an inert gas (such as nitrogen, argon) either a solution containing the whole or a portion of the various constituents, such as the compound to undergo hydrocyanation, .

SUMM [0084] If need be, a slight flushing of the reactor with an inert gas such as nitrogen or argon can be performed in order to expel the hydrogen cyanide which could still be present.

IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, Butadiene, reactions 110-59-8, Valeronitrile 110-83-8, Cyclohexene, reactions 111-69-3, Adiponitrile 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, Pentene-4-nitrile 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butenitrile 4553-62-2, 2-Methyl glutaronitrile 4635-87-4, 3-Pentenitrile 13284-42-9, 2-Pentenitrile 16529-56-9, 2-Methyl-3-butenitrile 17611-82-4, 2-Ethyl succinonitrile 25013-15-4, Methylstyrene 26588-32-9, Vinyl naphthalene (process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

SUMM [0064] In the context of discontinuous performance, there can be charged into a reactor, purged beforehand with an inert gas (such as nitrogen, argon) either a solution containing the whole or a portion of the various constituents, such as the compound to undergo hydrocyanation, the compounds of formulas (I) and (II), the transition metal compound, the possible reducing agent and solvent; or the said constituents separately. The reactor is generally then brought to the chosen temperature. The hydrogen cyanide is then introduced, preferably in a continuous and regular manner.

SUMM [0084] If need be, a slight flushing of the reactor with an inert gas such as nitrogen or argon can be performed in order to expel the hydrogen cyanide which could still be present.

IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, Butadiene, reactions 110-59-8, Valeronitrile 110-83-8, Cyclohexene, reactions 111-69-3, Adiponitrile 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, Pentene-4-nitrile 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butenitrile 4553-62-2, 2-Methyl glutaronitrile 4635-87-4, 3-Pentenitrile 13284-42-9, 2-Pentenitrile 16529-56-9, 2-Methyl-3-butenitrile 17611-82-4, 2-Ethyl succinonitrile 25013-15-4, Methylstyrene

10/586490

26588-32-9, Vinyl naphthalene  
(process of synthesis of compds. having nitrile functions from  
ethylenically unsatd. compds. using organophosphorus ligand-metal  
complexes)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
Butadiene, reactions 4635-87-4, 3-Pentenitrile  
(process of synthesis of compds. having nitrile functions from  
ethylenically unsatd. compds. using organophosphorus ligand-metal  
complexes)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



RN 4635-87-4 USPATFULL

CN 3-Pentenitrile (CA INDEX NAME)



L88 ANSWER 46 OF 60 USPATFULL on STN

ACCESSION . . .

for hydrocyanation of organic compounds comprising at least a ethylenical bond  
by reacting hydrogen cyanide, in the presence of a catalytic system  
comprising a transition metal and an organophosphorus ligand. The  
organophosphorus ligand is a compound with monophosphanorbornadiene  
structure. The invention. . .

AB . . . for hydrocyanation of organic compounds comprising at least a  
ethylenical bond by reacting hydrogen cyanide, in the presence of a  
catalytic system comprising a transition metal and an organophosphorus  
ligand. The organophosphorus ligand is a compound with  
monophosphanorbornadiene structure. The invention. . .

SUMM . . . addition of hydrocyanic acid to organic compounds having at  
least one ethylenic double bond in the presence of a nickel catalyst  
and a triaryl phosphite. This reaction can be carried out in the  
presence or absence of a solvent.

SUMM [0005] The catalyst employed is an organic nickel complex comprising  
ligands such as phosphines, arsines, stibines, phosphites, arsenites or  
antimonites.

SUMM [0006] The presence of a promoter for activating the catalyst, such as  
a boron compound or a metal salt, generally a Lewis acid, is also

- recommended in the said patent.
- SUMM [0009] This process makes possible correct hydrocyanation, in particular of butadiene and pentenenitriles, and easy separation of the catalytic solution by simple separation by settling and consequently prevents as far as possible discharge of effluents or waste comprising the metals acting as catalyst.
- SUMM [0010] However, research is being carried out to find novel catalytic systems which are more effective both as regards catalytic activity and as regards stability.
- SUMM . . . the present invention is to provide a novel family of ligands which makes it possible to obtain, with transition metals, catalytic systems exhibiting an improved activity with respect to the known systems.
- SUMM . . . hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand, characterized in that the ligand is a phosphine corresponding to the . . .
- SUMM [0065] The catalytic system used for the hydrocyanation according to the process of the invention can be prepared before its introduction into the . . . the appropriate amount of chosen transition metal compound and optionally of reducing agent. It is also possible to prepare the catalytic system "in situ" by simple addition of the phosphine and the transition metal compound to the hydrocyanation reaction medium, before. . .
- SUMM . . . batchwise implementation, it is in practice possible to charge to a reactor, purged beforehand using an inert gas (such as nitrogen or argon), either a solution comprising all or a portion of the various constituents, such as the phosphine, the transition metal compound, . . .
- SUMM . . . the hydrocyanation of the said nitrile compounds comprising ethylenic unsaturation by reaction with hydrogen cyanide and consists in using a catalytic system in accordance with the present invention with a cocatalyst comprising at least one Lewis acid.
- SUMM . . . of linear dinitrile with respect to all the dinitriles formed, and/or to increase the activity and the lifetime of the catalyst.
- SUMM [0087] As for the implementation of the basic process of the invention, the catalytic solution used for the hydrocyanation in the presence of Lewis acid can be prepared before its introduction into the reaction. . . transition metal compound, of the Lewis acid and optionally of the reducing agent. It is also possible to prepare the catalytic solution "in situ" by simple mixing of these various constituents.
- SUMM . . . the hydrocyanation process of the present invention and in particular by carrying out the hydrocyanation in the presence of the catalyst described above comprising at least one phosphine of formula (I) and at least one transition metal compound, to carry out, . . .
- SUMM [0092] In the context of this preferred alternative form, the catalytic system being already present for the reaction for the hydrocyanation of butadiene, it is sufficient to halt any introduction of. . .
- SUMM . . . it is possible, if appropriate, to carry out a slight flushing of the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.
- SUMM [0096] As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic system used for the isomerization can be prepared before its introduction into the reaction region, for example by addition, to. . . appropriate amount of chosen transition metal compound and optionally of the reducing agent. It is also possible to prepare the catalytic system "in situ" by simple

- mixing of these various constituents. The amount of transition metal compound and more particularly of. . .
- SUMM . . . the preparation of dinitrile compounds by hydrocyanation of an olefin such as butadiene can be carried out by using a catalytic system in accordance with the invention for the stages of formation of the unsaturated nitrites and the stage of isomerization. . . being possible for the reaction for the hydrocyanation of the unsaturated nitrites to dinitriles to be carried out with a catalytic system in accordance with the invention or any other catalytic system already known for this reaction.
- SUMM . . . the hydrocyanation of the olefin to unsaturated nitrites and the isomerization of the latter can be carried out with a catalytic system different from that of the invention, the stage of hydrocyanation of the unsaturated nitrites to dinitriles being carried out with a catalytic system in accordance with the invention.
- DETD . . . 5.0 eq of PNP or PNA ligand are charged to a reactor equipped with a stirrer and placed under an argon atmosphere. Approximately 1 ml (810 mg, d=0.81, M=81.12 g/mol) of degassed 2M3BN is added. The mixture is stirred and maintained. . .
- DETD . . . cosolvent or cosolvents and acetone cyanohydrin (30 eq) are successively introduced at ambient temperature into a Schlenk tube maintained under argon. The mixture is brought with stirring (600 rev/min) to 65° C. for 2 hours and then brought back to ambient. . .
- DETD . . . 56.5 mg (0.21 mmol, M=275 g/mol) of Ni(cod).sub.2 and 50.1 mg (0.21 mmol, M=242 g/mol) of BPh.sub.3 are charged under argon to a 20 ml Schott tube equipped with a septum. The mixture is brought with stirring to 65° C. and. . .
- CLM What is claimed is:
- . . . hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand, characterized in that the ligand is a phosphine corresponding to the. . .
- . . . ethylenic unsaturation by reaction with hydrogen cyanide, characterized in that the reaction is carried out in the presence of a catalytic system comprising at least one compound of a transition metal, at least one phosphine of formula (I) and a cocatalyst. . .
- . . . butadiene is carried out in the absence of hydrogen cyanide, the isomerization being carried out in the presence of a catalyst comprising at least one phosphine of formula (I) and at least one compound of a transition metal.
- IT 78-79-5, Isoprene, reactions 106-99-0, Butadiene, reactions 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 592-51-8P, 4-Pentenitrile 4403-61-6P, 2-Methyl-2-butenitrile 4635-87-4P, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 74-90-6, Hydrogen cyanide, reactions (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles using)
- PI US 2004063956 A1 20040401 <--|
- US 7098358 B2 20060829|
- AB The invention concerns a method for hydrocyanation of ethylenically unsaturated organic compounds into compounds comprising at least a nitrile function. More particularly, it concerns a method for hydrocyanation of

- organic compounds comprising at least a ethylenical bond by reacting hydrogen cyanide, in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand. The organophosphorus ligand is a compound with monophosphanorbornadiene structure. The invention concerns in particular hydrocyanation of butadiene into adiponitrile.]
- SUMM [0003] French Patent No. 1 599 761 discloses a process for the preparation of nitriles by addition of hydrocyanic acid to organic compounds having at least one ethylenic double bond in the presence of a nickel catalyst and a triaryl phosphite. This reaction can be carried out in the presence or absence of a solvent.
- SUMM [0005] The catalyst employed is an organic nickel complex comprising ligands such as phosphines, arsines, stibines, phosphites, arsenites or antimonites.
- SUMM [0006] The presence of a promoter for activating the catalyst, such as a boron compound or a metal salt, generally a Lewis acid, is also recommended in the said patent.
- SUMM [0009] This process makes possible correct hydrocyanation, in particular of butadiene and pentenenitriles, and easy separation of the catalytic solution by simple separation by settling and consequently prevents as far as possible discharge of effluents or waste comprising the metals acting as catalyst.
- SUMM [0010] However, research is being carried out to find novel catalytic systems which are more effective both as regards catalytic activity and as regards stability.
- SUMM [0011] One of the aims of the present invention is to provide a novel family of ligands which makes it possible to obtain, with transition metals, catalytic systems exhibiting an improved activity with respect to the known systems.
- SUMM [0012] To this end, the invention provides a process for the hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand, characterized in that the ligand is a phosphine corresponding to the following general formula: ##STR1##
- SUMM [0065] The catalytic system used for the hydrocyanation according to the process of the invention can be prepared before its introduction into the reaction region, for example by addition to the phosphine of formula (I), alone or dissolved in a solvent, of the appropriate amount of chosen transition metal compound and optionally of reducing agent. It is also possible to prepare the catalytic system "in situ" by simple addition of the phosphine and the transition metal compound to the hydrocyanation reaction medium, before or after the addition of the compound to be hydrocyanated.
- SUMM [0074] In the context of a batchwise implementation, it is in practice possible to charge to a reactor, purged beforehand using an inert gas (such as nitrogen or argon), either a solution comprising all or a portion of the various constituents, such as the phosphine, the transition metal compound, the possible reducing agent and the possible solvent, or the said constituents separately. Generally, the reactor is then brought to the chosen temperature and then the compound to be hydrocyanated is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and unvaryingly.

- SUMM [0076] An improvement to the process for the hydrocyanation of compounds comprising ethylenic unsaturation according to the present invention relates in particular to the hydrocyanation of the said nitrile compounds comprising ethylenic unsaturation by reaction with hydrogen cyanide and consists in using a catalytic system in accordance with the present invention with a cocatalyst comprising at least one Lewis acid.
- SUMM [0079] The Lewis acid used as cocatalyst makes it possible in particular, in the case of the hydrocyanation of aliphatic nitrites comprising ethylenic unsaturation, to improve the linearity of the dinitriles obtained, that is to say the percentage of linear dinitrile with respect to all the dinitriles formed, and/or to increase the activity and the lifetime of the catalyst.
- SUMM [0087] As for the implementation of the basic process of the invention, the catalytic solution used for the hydrocyanation in the presence of Lewis acid can be prepared before its introduction into the reaction region, for example by addition, to the reaction medium of the phosphine of formula (I), of the appropriate amount of chosen transition metal compound, of the Lewis acid and optionally of the reducing agent. It is also possible to prepare the catalytic solution "in situ" by simple mixing of these various constituents.
- SUMM [0088] It is also possible, under the conditions of the hydrocyanation process of the present invention and in particular by carrying out the hydrocyanation in the presence of the catalyst described above comprising at least one phosphine of formula (I) and at least one transition metal compound, to carry out, in the absence of hydrogen cyanide, isomerization of 2-methyl-3-butenitrile to pentenenitriles and more generally of branched unsaturated nitrites to linear unsaturated nitrites.
- SUMM [0092] In the context of this preferred alternative form, the catalytic system being already present for the reaction for the hydrocyanation of butadiene, it is sufficient to halt any introduction of hydrogen cyanide to allow the isomerization reaction to take place.
- SUMM [0093] In this alternative form, it is possible, if appropriate, to carry out a slight flushing of the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.
- SUMM [0096] As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic system used for the isomerization can be prepared before its introduction into the reaction region, for example by addition, to the reaction medium of the phosphine of formula (I), of the appropriate amount of chosen transition metal compound and optionally of the reducing agent. It is also possible to prepare the catalytic system "in situ" by simple mixing of these various constituents. The amount of transition metal compound and more particularly of nickel compound used and the amount of phosphine of formula (I) are the same as for the hydrocyanation reaction.
- SUMM [0098] However, the preparation of dinitrile compounds by hydrocyanation of an olefin such as butadiene can be carried out by using a catalytic system in accordance with the invention for the stages of formation of the unsaturated nitrites and the stage of isomerization above, it being possible for the reaction for the hydrocyanation of the unsaturated

nitrites to dinitriles to be carried out with a catalytic system in accordance with the invention or any other catalytic system already known for this reaction.

- SUMM [0099] Likewise, the reaction for the hydrocyanation of the olefin to unsaturated nitrites and the isomerization of the latter can be carried out with a catalytic system different from that of the invention, the stage of hydrocyanation of the unsaturated nitrites to dinitriles being carried out with a catalytic system in accordance with the invention.
- DETD [0124] 20 mg (0.073 mmol, M=275 g/mol, 1.0 eq) of Ni (cod).sub.2 and 5.0 eq of PNP or PNA ligand are charged to a reactor equipped with a stirrer and placed under an argon atmosphere. Approximately 1 ml (810 mg, d=0.81, M=81.12 g/mol) of degassed 2M3BN is added. The mixture is stirred and maintained at a temperature of 100° C. in a closed system for 1 hour. The reaction medium is cooled to ambient temperature (approximately 20° C.). The concentrations of the various constituents of the reaction medium are determined by analysis by GC (gas chromatography).
- DETD [0128] The ligand L (5 eq), 3PN (30 eq), Ni(cod).sub.2 (1 eq), ZnCl.sub.2 (1 eq), the degassed cosolvent or cosolvents and acetone cyanohydrin (30 eq) are successively introduced at ambient temperature into a Schlenk tube maintained under argon. The mixture is brought with stirring (600 rev/min) to 65° C. for 2 hours and then brought back to ambient temperature. 3 ml of acetone are introduced to neutralize the remaining HCN. The concentrations of the various components are determined by GC analysis in order to calculate the various degrees of conversion and of selectivity.
- DETD [0131] 0.506 g (6.25 mmol, M=81 g/mol) of 3PN, 340 mg (0.93 mmol, M=366 g/mol) of PNP, 1.96 g of degassed toluene, 56.5 mg (0.21 mmol, M=275 g/mol) of Ni(cod).sub.2 and 50.1 mg (0.21 mmol, M=242 g/mol) of BPh.sub.3 are charged under argon to a 20 ml Schott tube equipped with a septum. The mixture is brought with stirring to 65° C. and 531 mg (6.24 mmol, M=85 g/mol) of acetone cyanohydrin are injected via the septum and using a syringe driver at a flow rate of 0.19 ml/h. After reacting for 3 h, the mixture is brought back to ambient temperature and neutralized to remove the remaining HCN. The concentrations of the various components are determined by GC analysis in order to calculate the various degrees of conversion and of selectivity.
1. Process for the hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand, characterized in that the ligand is a phosphine corresponding to the following general formula (I): #STR11# in which: E represents O or S; n represents 0 or 1; R.sub.1, R.sub.4, R.sub.5 and R.sub.6, which are identical or different, represent a hydrogen atom; an optionally substituted, saturated or unsaturated, aliphatic hydrocarbonaceous radical comprising 1 to 40 carbon atoms, the hydrocarbonaceous chain of which is optionally interrupted by a heteroatom; an optionally substituted, monocyclic or polycyclic, saturated, unsaturated or aromatic, carbocyclic or heterocyclic radical; or a saturated or unsaturated, aliphatic hydrocarbonaceous radical, the hydrocarbonaceous chain of which is optionally interrupted by a heteroatom and carries a carbocyclic or heterocyclic radical as defined above, the said radical optionally being substituted; or else R.sub.4 and R.sub.5 form, together with the carbon atoms which carry them, an optionally substituted, saturated or unsaturated, carbocyclic monocycle preferably having from 5 to 7 carbon atoms; R.sub.2 represents a hydrogen atom or the X radical; R.sub.3 represents the X radical or the Y radical; it being understood that one and one alone of the R.sub.2



and R.sub.3 substituents represents the X radical; X being chosen from a monocyclic or bicyclic, aromatic carbocyclic or heterocyclic radical having from 2 to 20 carbon atoms; a 1-alkenyl radical optionally exhibiting one or more additional unsaturations in the hydrocarbonaceous chain and having from 2 to 12 carbon atoms; a 1-alkynyl radical optionally exhibiting one or more additional unsaturations in the hydrocarbonaceous chain and having from 2 to 12 carbon atoms; or a --CN, [(C.sub.1-C.sub.12)alkyl]-carbonyl, [(C.sub.3-C.sub.18)aryl]carbonyl, [(C.sub.1-C.sub.12)alkoxy]-carbonyl, [(C.sub.6-C.sub.18)aryloxy]carbonyl, carbamoyl, [(C.sub.1-C.sub.12)alkyl]carbamoyl or [di(C.sub.1-C.sub.12) alkyl]carbamoyl radical; and Y taking any one of the meanings of R.sub.1, with the exception of a hydrogen atom; R.sub.7 has the meaning of R.sub.1, R.sub.4, R.sub.5 and R.sub.6 or represents a hydrocarbonaceous radical comprising a carbonyl functional group or a radical of following formulae: ##STR12## in which, A represents a hydrogen atom; (C.sub.1-C.sub.10)alkyl; or (C.sub.6-C.sub.10)aryl or (C.sub.6-C.sub.10)aryl(C.sub.1-C.sub.10)alkyl in which the aryl part is optionally substituted by one or more radicals chosen from (C.sub.1-C.sub.6)alkyl, (C.sub.1-C.sub.6)alkoxy, trifluoromethyl, halogen, di(C.sub.1-C.sub.6)alkylamino, (C.sub.1-C.sub.6) alkoxycarbonyl, carbamoyl, (C.sub.1-C.sub.6)alkylaminocarbonyl and di(C.sub.1-C.sub.6) alkylaminocarbonyl; --Ar.sub.1--Ar.sub.2-- represent: either the divalent radical of formula: ##STR13## in which each of the phenyl nuclei is optionally substituted by one or more Z groups as defined below; or the divalent radical of formula: ##STR14## in which each of the phenyl nuclei is optionally substituted by one or more Z groups as defined below; Z represents (C.sub.1-C.sub.6)alkyl, (C.sub.1-C.sub.6)alkoxy, trifluoromethyl, halogen, (C.sub.1-C.sub.6)alkoxycarbonyl, di(C.sub.1-C.sub.6)alkylamino, (C.sub.1-C.sub.6)alkylaminocarbonyl or di(C.sub.1-C.sub.6)alkylaminocarbonyl; R.sub.8 and R.sub.9, which are identical or different, represent a substituted or unsubstituted aryl radical.

11. Process according to one of the preceding claims for the hydrocyanation to dinitriles of nitrile compounds comprising ethylenic unsaturation by reaction with hydrogen cyanide, characterized in that the reaction is carried out in the presence of a catalytic system comprising at least one compound of a transition metal, at least one phosphine of formula (I) and a cocatalyst comprising at least one Lewis acid.

18. Process according to one of claims 1 to 17, characterized in that the isomerization to pentenenitriles of the 2-methyl-3-butenitrile present in the reaction mixture originating from the hydrocyanation of butadiene is carried out in the absence of hydrogen cyanide, the isomerization being carried out in the presence of a catalyst comprising at least one phosphine of formula (I) and at least one compound of a transition metal.

- IT 78-79-5, Isoprene, reactions 186-99-0, Butadiene, reactions 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 592-51-8P, 4-Pentenitrile 4403-61-6P, 2-Methyl-2-butenitrile 4635-87-4E, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 74-90-8, Hydrogen cyanide, reactions

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(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles using)  
IT 106-99-0, Butadiene, reactions  
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)  
RN 106-99-0 USPATFULL  
CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4E, 3-Pentenitrile  
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)  
RN 4635-87-4 USPATFULL  
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions  
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles using)  
RN 74-90-8 USPATFULL  
CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 47 OF 60 USPATFULL on STN  
ACCESSION NUMBER: 2004:70877 USPATFULL [Full-text](#)  
TITLE: Phosphorus-containing compositions and their use in hydrocyanation, isomerization and hydroformylation reactions  
INVENTOR(S): Gagne, Michel R., Carrboro, NC, UNITED STATES  
Moloy, Kenneth G., Hockessin, DE, UNITED STATES  
Radu, Nora S., Landenberg, PA, UNITED STATES  
Santora, Brian P., River Falls, WI, UNITED STATES  
Tam, Wilson, Boothwyn, PA, UNITED STATES

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 2004054105	A1	20040318
	US 6924345	B2	20050802
APPLICATION INFO.:	US 2003-659205	A1	20030910 (10)
RELATED APPLN. INFO.:	Division of Ser. No. US 2001-994135, filed on 26 Nov 2001, GRANTED, Pat. No. US 6660876		
DOCUMENT TYPE:	Utility		

FILE SEGMENT: APPLICATION  
 LEGAL REPRESENTATIVE: E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT  
 RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417  
 LANCASTER PIKE, WILMINGTON, DE, 19805

NUMBER OF CLAIMS: 45  
 EXEMPLARY CLAIM: 1  
 LINE COUNT: 2484

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A polymeric, phosphorus-containing composition made by heating, in the presence of an initiator, preferably a free radical initiator, and optionally in the presence of one or more comonomers, at least one substituted phosphonylated 2,2'-dihydroxyl-1,1'-binaphthalene or at least one substituted 2,2'-dihydroxyl-1,1'-biphenylene.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted, ethylenically unsaturated, organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile, . . .

SUMM . . . into a reactor, such as a tubular reactor, taking care to avoid exposure of oxygen-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and. . .

SUMM . . . herein, a non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used, if desired, at the expense of loss of a proportion of the catalyst activity through oxidation. Impurities. . .

SUMM . . . in a thermostatically controlled oil bath. HCN was delivered to the flask as an HCN/N.sub.2 gas mixture by bubbling dry nitrogen carrier gas through liquid HCN maintained in an ice bath at 0° C. This provided a vapor stream that was about 35% by volume HCN. The rate of nitrogen gas flow determined the rate of HCN delivery. Samples were periodically analyzed by gas chromatography (GC).

DETD [0161] Aspect 2: Preparation of ethylenically unsaturated, phosphorus-containing bidentate ligand (1): Under nitrogen atmosphere, a 100 mL flask with magnetic stir bar was charged with 2.450 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.865 grams of acryloyl. . .

DETD [0206] Aspect 2: Preparation of ethylenically unsaturated ligand (8): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 1.880 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.664 grams of acryloyl chloride, . . .

DETD . . . and 5 mL of 3PN in a closed reactor was placed in a 50° C. oil bath and HCN saturated nitrogen was delivered at a nitrogen flow rate of 24 cc/min. The reaction was heated at 50° C. for 1 hour and then at 70° C. for 30 minutes. Nitrogen flow was decreased to 12 cc/min. and the reaction was run at 70° C. for an additional 90 minutes. The. . .

DETD [0230] Aspect 2: Preparation of ethylenically unsaturated ligand (12): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 0.931 grams of the monoacrylate of 2,2-bis(4-hydroxy-3-methylphenyl)propane (prepared from. . .

DETD . . . to the mixture. The mixture was heated in a 50° C. oil

- bath and HCN was delivered with 24 cc/min. nitrogen flow rate. After 90 minutes of reaction, GC analysis indicated 57.6% conversion of 3PN with 92% selectivity to ADN. To. . . but the reaction was allowed to continue at 50° C. for 120 minutes. The mixture was allowed to sit under nitrogen at room temperature overnight. GC analysis indicated 62% conversion of 3PN with 91.3% selectivity to ADN.
- DETD . . . begin an additional reaction. The reaction was placed in a 70° C. oil bath and HCN was delivered with a nitrogen flow rate of 30 cc/min. The reaction was then stored at room temperature overnight. The mixture was then heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 30 minutes. GC analysis indicated 75% conversion of 3PN with selectivity to ADN of. . . was added 5 mL of 3PN. The mixture was heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 210 minutes. GC analysis indicated 65% conversion of 3PN with selectivity to ADN of. . .
- DETD [0246] Aspect 2: Preparation of the diphosphite ligand (13): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.2O (5 mL) solution of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.051 g, 1.5x10.sup.-4 mol) and Et.sub.3N (0.040, 3.9x10.sup.-4 mol) was. . .
- DETD [0248] Aspect 3: Polymerization of the ethylenically unsaturated compound (13) with divinylbenzene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.027 g, 2.7x10.sup.-5 mol) described in. . .
- DETD [0251] Aspect 2: Preparation of ethylenically unsaturated diphosphite ligand (14): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.2O (5 mL) solution of 3,3',4,4',5,5',6,6'-octamethyl-2,2'-dihydroxy-1,1'-biphenyl (0.100 g, 0.67 mmol) and Et.sub.3N (0.152 g, 1.5 mmol). . .
- DETD [0252] Aspect 3: Polymerization of the ethylenically unsaturated compound (14) with divinylbenzene and styrene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.100 g, 0.09 mmol) described in. . .
- DETD [0255] Aspect 5.1: Polymerization of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl with styrene: Under nitrogen atmosphere, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.500 g, 1.48 mmol), AIBN (0.040). . .
- DETD [0256] Aspect 5.2: Formation of the diphosphite ligand from the polymeric precursor of Example 15: Under nitrogen atmosphere, a cold solution (-30° C.) of o-cresol (0.027 g, 0.25 mmol) in toluene (5 mL) was added to a. . .
- DETD . . . mL of 3PN. The mixture was heated in a 70 C oil bath and HCN was delivered with 12 cc/min. nitrogen flow rate. After 180 minutes, GC indicated 93.9% conversion to dinitrile with ADN selectivity of 88.4%.
- IT 106-99-0, Butadiene, reactions 4635-87-4,  
3-Pentenitrile  
(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns.  
and  
their use in hydrocyanation, isomerization and hydroformylation reactions)
- IT 74-85-1, Ethylene, reactions 74-98-8, Hydrogen cyanide,  
reactions 79-97-0, 2,2-Bis(4-hydroxy-3-methylphenyl)propane 814-68-6,  
Acryloyl chloride 7719-12-2, Phosphorus trichloride 13185-00-7,  
6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthyl 26567-10-2 31860-10-3

50291-18-4 100930-72-1 532941-08-5 538345-81-2 538346-27-9  
538346-36-0

(manufacture of unsatd. phosphorus-containing compns. and their use in hydrocyanation, isomerization and hydroformylation reactions)

SUMM [0138] The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted, ethylenically unsaturated, organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, 7-octen-1-ol, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol, 3-pentenal, 4-pentenal, and combinations of two or more thereof.

SUMM [0147] The hydroformylation process can be run in solution or in the gas phase. When the hydroformylation is carried out in the vapor phase, the preferred temperature range is from about 50° C. to about 180° C., most preferably from about 90° C. to 110° C. The temperature must be chosen high enough so as to maintain all of the reactants and products in the vapor phase, but low enough to prevent deterioration of the catalyst. The particular preferred temperature depends to some extent on the catalyst being used, the olefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical and can be from about 0.1 to 1.0 MPa. The pressure and temperature combination must be chosen so as to maintain reactants and products in the vapor phase. A given catalyst is loaded into a reactor, such as a tubular reactor, taking care to avoid exposure of oxygen-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and are conveniently recovered by cooling. The reactor effluent can be directly connected to a sampling valve and can be analyzed by gas chromatography. Aldehydic products, such as linear and branched butyraldehydes obtained from hydroformylation of propylene, can be quantitatively separated and analyzed using a 30M DB-Wax® capillary GC column.

SUMM [0148] For the hydrocyanation, isomerization, and hydroformylation processes described herein, a non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used, if desired, at the expense of loss of a proportion of the catalyst activity through oxidation. Impurities that are detrimental to the catalyst should be kept to a minimum.

SUMM [0159] Hydrocyanation of 3-pentenitrile was also performed by slowly adding the HCN to the reaction mixture. The catalyst composition and 3-pentenitrile were heated in a thermostatically controlled oil bath. HCN was delivered to the flask as an HCN/N<sub>2</sub> sub.2 gas mixture by bubbling dry nitrogen carrier gas through liquid HCN maintained in an ice bath at 0° C. This provided a vapor stream that was about 35% by volume HCN. The rate of nitrogen gas flow determined the rate of HCN delivery. Samples were periodically analyzed by gas chromatography (GC).

DETD [0161] Aspect 2: Preparation of ethylenically unsaturated, phosphorus-containing bidentate ligand (1): Under nitrogen atmosphere, a 100 mL flask with magnetic stir bar was charged with 2.450 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.865 grams of acryloyl

chloride, 40 mL of toluene and 8 mL of THF. The mixture was cooled to -30° C. and 1.2 grams of triethylamine in 15 mL of toluene was added. About a quarter of the solvent was removed under vacuum and the mixture cooled to -30° C. To this mixture was added 2.266 grams of the phosphorodichlorodite of 2-isopropylphenol and 1.2 grams of triethylamine in 10 mL of toluene. The mixture was stirred for one and one-half hours and cooled to -30° C. To the mixture was added 1.157 grams of 3,3',5,5'-tetramethyl-2,2'-biphenol and 1.2 grams of triethylamine. The mixture was kept at -30° C. overnight and then filtered. Solvent was removed to give 5.978 grams of a tacky brown solid (.sup.31P NMR in CDCl.sub.3: 142.21, 142.15, 135.20, 135.11, 134.74, 134.29, 132.01, 131.96, and 131.13).

DETD [0206] Aspect 2: Preparation of ethylenically unsaturated ligand (8): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 1.880 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.664 grams of acryloyl chloride, and 40 mL of THF. The mixture was cooled to -30° C. and a pre-cooled solution (at -30° C.) containing 1 gram of triethylamine in 15 mL of THF was added. The THF was removed under vacuum and the residue dissolved in 50 mL of THF. To this slurry was added 0.503 grams of phosphorus trichloride. The mixture was cooled to -30° C. and a pre-cooled solution containing 0.5 gram of triethylamine in 10 mL of THF was added. After stirring for several days, 0.598 grams of 3,3'-diisopropyl-5,5',6,6'-tetramethyl-2,2'-biphenol was added along with 1.2 grams of triethylamine. The mixture was stirred for forty minutes, filtered and the solvent was removed under vacuum to give 3.146 grams of a yellow solid (.sup.31P NMR (CDCl.sub.3): 135.58, 135.25, 135.18, 134.80, 134.71, 132.71, 131.90, 130.80, 127.94, and 127.87).

DETD [0229] Aspect 10: Semibatch 3-pentenitrile hydrocyanation using nickel catalyst: A reaction mixture of 0.567 grams of the above catalyst, 0.027 grams of zinc chloride, 5 mL of toluene and 5 mL of 3PN in a closed reactor was placed in a 50° C. oil bath and HCN saturated nitrogen was delivered at a nitrogen flow rate of 24 cc/min. The reaction was heated at 50° C. for 1 hour and then at 70° C. for 30 minutes. Nitrogen flow was decreased to 12 cc/min. and the reaction was run at 70° C. for an additional 90 minutes. The temperature was then increased to 80° C. and the reaction was continued for another 90 minutes. GC analysis indicated 68% conversion of 3-pentenitrile to dinitrile with an ADN selectivity of 89%.

DETD [0230] Aspect 2: Preparation of ethylenically unsaturated ligand (12): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 0.931 grams of the monoacrylate of 2,2-bis(4-hydroxy-3-methylphenyl)propane (prepared from the reaction of acryloyl chloride with 2,2-bis(4-hydroxy-3-methylphenyl)propane), 0.627 grams of the phosphorodichloridite of o-cresol, and 40 mL of toluene. The mixture was cooled to -30° C. and a precooled solution (at -30° C.) containing 0.4 grams of triethylamine in 15 mL of toluene was added. After stirring for 2 hours, .sup.31P NMR in CDCl.sub.3 indicated a peak at 162.8 ppm. The mixture was cooled to -30° C. and 0.448 grams of 3,3',4,4',5,5'-hexamethyl-2,2'-biphenol and 0.65 grams of triethylamine in 2 mL of THF were added. After stirring overnight, the mixture was filtered and the THF removed under vacuum to give a yellow solid. The solid was dissolved in 10 mL of toluene and 0.8 grams of triethylamine was added in 5 mL of THF. The mixture was stirred overnight and filtered. The solvent was removed. .sup.31P NMR indicated some phosphorodichloridite still present. The residue was dissolved in THF and 0.75 grams of triethylamine were added. After stirring overnight, the mixture was filtered through silica gel, and the solvent was removed under vacuum. 1.225 Grams of yellow solid were recovered

- (.sup.31P NMR in CDCl<sub>3</sub>.sub.3: 137.47, 137.31, 135.29, 135.21, 135.15, 135.00, 134.82, 134.73, 134.40, 134.31, 133.41, 133.40, 132.07, 131.98, 130.44, 127.74, and 127.69).
- DETD [0238] Aspect 10: Hydrocyanation of 3-pentenitrile: 29 milligrams of ZnCl<sub>2</sub>.sub.2 and 5 mL of 3PN were added to the mixture. The mixture was heated in a 50° C. oil bath and HCN was delivered with 24 cc/min. nitrogen flow rate. After 90 minutes of reaction, GC analysis indicated 57.6% conversion of 3PN with 92% selectivity to ADN. To the mixture was added 5 mL of 3PN and the reaction was continued for 90 minutes. At this point, HCN delivery was stopped but the reaction was allowed to continue at 50° C. for 120 minutes. The mixture was allowed to sit under nitrogen at room temperature overnight. GC analysis indicated 62% conversion of 3PN with 91.3% selectivity to ADN.
- DETD [0239] Ligand recycle: At this time, the solvent was removed via syringe from the reactor. 5 mL of toluene, 5 mL of 3PN and 29 milligrams of ZnCl<sub>2</sub>.sub.2 were added to begin an additional reaction. The reaction was placed in a 70° C. oil bath and HCN was delivered with a nitrogen flow rate of 30 cc/min. The reaction was then stored at room temperature overnight. The mixture was then heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 30 minutes. GC analysis indicated 75% conversion of 3PN with selectivity to ADN of 92.2%. To this mixture was added 5 mL of 3PN. The mixture was heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 210 minutes. GC analysis indicated 65% conversion of 3PN with selectivity to ADN of 91.8%.
- DETD [0246] Aspect 2: Preparation of the diphosphite ligand (13): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.20 (5 mL) solution of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.051 g, 1.5x10<sup>-4</sup> mol) and Et.sub.3N (0.040, 3.9x10<sup>-4</sup> mol) was slowly added to a Et.sub.20 (5 mL) solution of phosphorochlorodite of 2-isopropoxyphenol (0.140 g, 3.9x10<sup>-4</sup> mol). The solution was allowed to warm up to room temperature and was stirred for one hour. The reaction mixture was filtered through celite and alumina. The volatiles were evaporated to yield a white powder in 67% yield. (0.100 g).
- DETD [0248] Aspect 3: Polymerization of the ethylenically unsaturated compound (13) with divinylbenzene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.027 g, 2.7x10<sup>-5</sup> mol) described in example 13, AIBN (0.002 g), DVB (0.1900 g) and THF (0.184 g). This vial was screwed shut and placed in a 70° C. oil bath for 24 hours. After polymerization, the polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (0.350 g) was insoluble in all organic solvents. Elemental analysis: P found: 1.51%.
- DETD [0251] Aspect 2: Preparation of ethylenically unsaturated diphosphite ligand (14): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.20 (5 mL) solution of 3,3',4,4',5,5',6,6'-octamethyl-2,2'-dihydroxy-1,1'-biphenyl (0.100 g, 0.67 mmol) and Et.sub.3N (0.152 g, 1.5 mmol) was slowly added to an Et.sub.20 (5 mL) solution of phosphorochlorodite of trans-2-ethoxy-5-(1-propenyl)phenol (0.631 g, 1.5 mmol). The solution was allowed to warm to room temperature and was stirred for one hour. The reaction mixture was filtered through celite and alumina. The volatiles were evaporated to give 86% yield of a white powder (0.623 g).
- DETD [0252] Aspect 3: Polymerization of the ethylenically unsaturated compound (14) with divinylbenzene and styrene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.100 g, 0.09 mmol) described

in example 14, AIBN (0.005 g), DVB (0.40 g), styrene (0.70 g) and THF (1.5 mL). This vial was screwed shut and placed in a 70° C. oil bath for 48 hours, after which DVB (0.75 g) and AIBN (0.005 g) were added and the vial was returned to the oil bath. After 48 hours, the opaque polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (0.137 g) was insoluble in all organic solvents.

DETD [0255] Aspect 5.1: Polymerization of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl with styrene: Under nitrogen atmosphere, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.500 g, 1.48 mmol), AIBN (0.040 g), styrene (4.0 mL) and THF (4.0 mL). The vial was screwed shut and placed in a 70° C. oil bath for 24 hours. After polymerization, the polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (4.8 g) was insoluble in all organic solvents.

DETD [0256] Aspect 5.2: Formation of the diphosphite ligand from the polymeric precursor of Example 15: Under nitrogen atmosphere, a cold solution (-30° C.) of o-cresol (0.027 g, 0.25 mmol) in toluene (5 mL) was added to a solution of the phosphorodichlorodite of phenol (0.045 g, 0.25 mmol) and n-Bu.sub.3N (0.047 g, 0.25 mmol) in toluene (5 mL). The resulting mixture was allowed to stir at room temperature for 1.5 hours, after which it was cooled to -30° C. This cold solution was added to a cold slurry of polymer from example 15 (0.328 g, 0.10 mmol) and n-Bu.sub.3N (0.047 g, 0.25 mmol) in toluene (5 mL). This mixture was stirred at room temperature for five hours. The polymer product was isolated by filtration and washed with toluene and acetonitrile. After drying under vacuum, a tacky solid (0.350 g) was obtained.

DETD [0269] Aspect 10: Semi-batch hydrocyanation of 3-pentenitrile: To 0.388 g of the catalyst from Example 18B was added 19 mg of zinc chloride and 5 mL of 3PN. The mixture was heated in a 70 C oil bath and HCN was delivered with 12 cc/min. nitrogen flow rate. After 180 minutes, GC indicated 93.9% conversion to dinitrile with ADN selectivity of 88.4%.

IT 106-99-0, Butadiene, reactions 4635-87-4,  
3-Pentenitrile  
(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns.

and  
their use in hydrocyanation, isomerization and hydroformylation reactions)

IT 74-85-1, Ethylene, reactions 74-90-8, Hydrogen cyanide,  
reactions 79-97-0, 2,2-Bis(4-hydroxy-3-methylphenyl)propane 814-68-6,  
Acryloyl chloride 7719-12-2, Phosphorus trichloride 13185-00-7,  
6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthyl 26567-10-2 31860-10-3  
50291-18-4 100930-72-1 532941-08-5 538345-81-2 538346-27-9  
538346-36-0

(manufacture of unsatd. phosphorus-containing compns. and their use in hydrocyanation, isomerization and hydroformylation reactions)

IT 106-99-0, Butadiene, reactions 4635-87-4,  
3-Pentenitrile  
(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns.

and  
their use in hydrocyanation, isomerization and hydroformylation reactions)

RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



10/586490



RN 4635-87-4 USPATFULL  
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-6, Hydrogen cyanide, reactions  
(manufacture of unsatd. phosphorus-containing compns. and their use in  
hydrocyanation, isomerization and hydroformylation reactions)  
RN 74-90-8 USPATFULL  
CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 48 OF 60 USPATFULL on STN  
ACCESSION NUMBER: 2003:301062 USPATFULL Full-text  
TITLE: Phosphonite ligands and their use in hydrocyanation  
INVENTOR(S): Lenges, Christian P., Wilmington, DE, UNITED STATES  
Lu, Helen S. M., Wallingford, PA, UNITED STATES  
Ritter, Joachim C., Wilmington, DE, UNITED STATES

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2003212288	A1	20031113	<--
	US 6846945	B2	20050125	
APPLICATION INFO.:	US 2003-454024	A1	20030604	(10)
RELATED APPLN. INFO.:	Division of Ser. No. US 2002-93655, filed on 7 Mar 2002, PENDING			
DOCUMENT TYPE:	Utility			
FILE SEGMENT:	APPLICATION			
LEGAL REPRESENTATIVE:	E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805			
NUMBER OF CLAIMS:	10			
EXEMPLARY CLAIM:	1			
LINE COUNT:	411			

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM [0002] The present invention concerns the use of catalyst compositions

- comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.
- SUMM [0003] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.
- SUMM [0004] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.
- SUMM [0005] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . . .
- SUMM [0007] The use of a catalyst based on a ligand of structure III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.
- SUMM . . . present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR2##
- SUMM [0011] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure III as described. . . .
- SUMM . . . VIII metal or a compound thereof is combined with at least one of the ligand structure III to provide the catalyst. Among the Group VIII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by. . . .
- SUMM [0013] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni(P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3).sub.3. . . .
- SUMM [0014] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the. . . of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or. . . .
- SUMM . . . at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.
- SUMM [0018] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a

nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a . .

- SUMM . . . a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to. . .
- SUMM [0020] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the. . .
- SUMM [0021] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.
- SUMM . . . The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran. . .
- SUMM [0024] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to. . .
- SUMM . . . in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting. . . U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3, and (C.sub.6H.sub.5).sub.3Sn(CF.sub.3SO.sub.3).sub.3, CH.sub.3C.sub.6H.sub.5SO.sub.3, or (C.sub.6H.sub.5).sub.3BCN. The mole ratio of promoter to Group. . .
- SUMM [0038] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitrites. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees. . .
- DETD [0039] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following. . .
- DETD [0040] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1.1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1.1:1. The molar. . .
- DETD [0045] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.
- DETD [0047] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14 g of the HCN solution. The. . .
- CLM What is claimed is:
- . . . 1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a

catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . . .  
 10. The use of a catalyst based on a ligand of structure III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

- IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenitrile 1635-87-4P  
 , 3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile  
 (phosphonite ligands and their use in hydrocyanation)
- IT 16529-56-9P, 2-Methyl-3-butenitrile 16529-66-1P,  
 trans-3-Pentenitrile  
 (phosphonite ligands and their use in hydrocyanation)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 (phosphonite ligands and their use in hydrocyanation)
- PI US 2003212288 A1 20031113 <--|  
 US 6846945 B2 20050125|
- SUMM [0002] The present invention concerns the use of catalyst compositions comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.
- SUMM [0003] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.
- SUMM [0004] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.
- SUMM [0005] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR1##
- SUMM [0007] The use of a catalyst based on a ligand of structure III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.
- SUMM [0008] The present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR2##
- SUMM [0011] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure III as described above and optionally a Lewis acid.

- SUMM [0012] Generally, a Group VIII metal or a compound thereof is combined with at least one of the ligand structure III to provide the catalyst. Among the Group VIII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by the ligand structure of the present invention is the most preferred source of Group VIII metal or Group VIII metal compound.
- SUMM [0013] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.3 and Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.2(C.sub.2H.sub.4), all of which are known in the art.
- SUMM [0014] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the ligand of structure III of the present invention in a ratio of nickel:bidentate ligand of 1:1. The ligand may be combined with nickel in a solvent, or preferably in the substrate medium. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions.
- SUMM [0016] The divalent nickel compound is combined with the ligand structure III of the present invention in a suitable solvent, preferably the unsaturated olefin, in a ratio of 1:1, or preferably at least 2:1. The combination is then combined with a suitable reducing agent at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.
- SUMM [0018] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a promoter. As used herein, the term "fluid" means gas, a liquid, or a combination of these. Any fluid containing about 1 to 100% HCN can be used.
- SUMM [0019] A particularly significant use of the ligands of the present invention is in the hydrocyanation of olefins. In such a process, an olefinic compound such as a diolefinic compound can be converted to a nitrile or a dinitrile, or a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to form the mixture. However, it is preferred that HCN be added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the vessel. As an alternative, a cyanohydrin can be used as the source of

HCN. See, for example, U.S. Pat. No. 3,655,723, incorporated herein by reference.

- SUMM [0020] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.
- SUMM [0021] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.
- SUMM [0023] The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitrites such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in the gas phase.
- SUMM [0024] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to about 200° C. can be used with the range of 0° C. to 150° C. being preferred.
- SUMM [0031] The process of this invention can be carried out in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include, but are not limited to, ZnBr.sub.2, ZnI.sub.2, ZnCl.sub.2, ZnSO.sub.4, CuCl.sub.2, CuCl, Cu(O.sub.3SCF.sub.3).sub.2, CoCl.sub.2, CoI.sub.2, FeI.sub.2, FeCl.sub.3, FeCl.sub.2, FeCl.sub.2(THF).sub.2, TiCl.sub.2, TiCl.sub.4 (THF).sub.2, MnCl.sub.2, ScCl.sub.3, AlCl.sub.3, (C.sub.8H.sub.17)AlCl.sub.2, (C.sub.8H.sub.17).sub.2AlCl, (iso-C.sub.4H.sub.9).sub.2AlCl, Ph.sub.2AlCl, PhAlCl.sub.2, ReCl.sub.5, ZrCl.sub.4, NbCl.sub.5, VCl.sub.3, CrCl2, MoCl.sub.5, YCl.sub.3, CdCl.sub.2, LaCl.sub.3, Er(O.sub.3SCF.sub.3).sub.3, Yb(O.sub.2CCF.sub.3).sub.3, SmCl.sub.3, B(C.sub.6H.sub.5).sub.3, TaCl.sub.5. Suitable promoters known in the art. These include metal salts, such as ZnCl.sub.2, CoI.sub.2, and SnCl.sub.2, and organometallic compounds (such as R.sub.8AlCl.sub.2, R.sub.8SnO.sub.3SCF.sub.3, and R.sub.8B, where R.sub.8 is an alkyl or aryl group). U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3, and (C.sub.6H.sub.5).sub.3Sn(CF.sub.3SO.sub.3), CH.sub.3C(C.sub.6H.sub.5)SO.sub.3, or (C.sub.6H.sub.5).sub.3BCN. The mole ratio of promoter to Group VIII metal present in the reaction can be within the range of about 1:16 to about 50:1.

SUMM [0038] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitrites. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees C. to 150 degrees C., and preferably from 80 degrees C. to 120 degrees C. A solvent may be used. Examples of a suitable solvent include but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof.

DETD [0039] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.

DETD [0040] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1.1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1.1:1. The molar ratio of trans-3PN to Ni was 200 equivalents. The reaction vessel was heated to the temperature as described in the following Tables and hydrogen cyanide was delivered by slow evaporation of the hydrogen cyanide from a reservoir connected to the reaction vessel by a feed tube in an otherwise closed reaction system. The reaction was analyzed after 15 hours. The reaction mixture was analyzed using standard Gas Chromatograph methodology. Tables I-through III list the conversion of pentenenitriles to dinitriles and the selectivity to adiponitrile, defined as the ratio of adiponitrile over all dinitriles, in this hydrocyanation reaction.

TABLE I

Promoter: ZnCl.sub.2

Conversion	Selectivity ligand	to
Dinitrile	to ADN	
50° C.		
Example 1	##STR6##	73.8
91.0		
Example 2	##STR7##	2.2
81.8		
Example 3	##STR8##	57.4
90.6		
Example 4	##STR9##	32.7
87.6		
Example 5	##STR10##	87.5
88.7		
Example 6	##STR11##	28.2
85.1		
80° C.		
Example 7	##STR12##	13.5
82.9		

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Example 8      ##STR13##      58.8  
73.0

Example 9      ##STR14##      66.0  
77.2

Example 10     ##STR15##      83.2  
73.7

DETD [0045] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.

DETD [0047] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14 g of the HCN solution. The vessel was sealed and placed in a reactor set at 100° C. Samples were removed after three hours.

1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR28## wherein X and Q are as described in Formula II, and L is a linking group selected from the group consisting of -CR1 R2--, --O--, --S--, --CO-- (wherein each of R1-R2 are independent of one another, are a hydrogen atom, a C1-12 alkyl group, or an aryl group), and each of m and m' which are independent of each other, are 0 or 1.

10. The use of a catalyst based on a ligand of structure III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenitrile 4635-87-4P  
, 3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile  
(phosphonite ligands and their use in hydrocyanation)

IT 16529-56-9P, 2-Methyl-3-butenitrile 16529-66-1P,  
trans-3-Pentenitrile  
(phosphonite ligands and their use in hydrocyanation)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
(phosphonite ligands and their use in hydrocyanation)

IT 4635-87-4P, 3-Pentenitrile 16545-78-1P,  
cis-3-Pentenitrile  
(phosphonite ligands and their use in hydrocyanation)

RN 4635-87-4 USPATFULL

CN 3-Pentenitrile (CA INDEX NAME)



RN 16545-78-1 USPATFULL

CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.

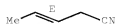


10/586490



IT 16529-66-1E, trans-3-Pentenitrile  
 (phosphonite ligands and their use in hydrocyanation)  
 RN 16529-66-1 USPATFULL  
 CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 (phosphonite ligands and their use in hydrocyanation)  
 RN 74-90-8 USPATFULL  
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL  
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 49 OF 60 USPATFULL on STN  
 ACCESSION NUMBER: 2003:277345 USPATFULL Full-text  
 TITLE: Phosphonite ligands and their use in hydrocyanation  
 INVENTOR(S): Lenges, Christian P., Wilmington, DE, UNITED STATES  
 Lu, Helen S. M., Wallingford, PA, UNITED STATES  
 Ritter, Joachim C., Wilmington, DE, UNITED STATES

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2003195372	A1	20031016	<--
	US 6737539	B2	20040518	
APPLICATION INFO.:	US 2003-454074	A1	20030604	(10)
RELATED APPLN. INFO.:	Division of Ser. No. US 2002-93655, filed on 7 Mar 2002, PENDING			
DOCUMENT TYPE:	Utility			
FILE SEGMENT:	APPLICATION			
LEGAL REPRESENTATIVE:	E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT			

RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417  
LANCASTER PIKE, WILMINGTON, DE, 19805

NUMBER OF CLAIMS: 10  
EXEMPLARY CLAIM: 1  
LINE COUNT: 415

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM [0002] The present invention concerns the use of catalyst compositions comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.

SUMM [0003] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.

SUMM [0004] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.

SUMM [0005] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . .

SUMM [0007] The use of a catalyst based on a ligand of structure II for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

SUMM . . . present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR2##

SUMM [0011] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure II I as. . .

SUMM . . . VII metal or a compound thereof is combined with at least one of the ligand structure II to provide the catalyst. Among the Group VII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by. . .

SUMM [0013] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni(P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3).sub.3. . .

- SUMM [0014] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the . . . of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or. . .
- SUMM . . . at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.
- SUMM [0018] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a. . .
- SUMM . . . a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to. . .
- SUMM [0020] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the. . .
- SUMM [0021] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.
- SUMM . . . The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran. . .
- SUMM [0024] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to. . .
- SUMM . . . in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting. . . U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3, and (C.sub.6H.sub.5).sub.3Sn(CF.sub.3SO.sub.3).sub.3, CH.sub.3C(C.sub.6H.sub.5)SO.sub.3, or (C.sub.6H.sub.5).sub.3BCl. The mole ratio of promoter to Group. . .
- SUMM [0038] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitrites. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees. . .
- DETD [0039] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following. . .

- DETD [0040] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1.1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1.1:1. The molar. . . .
- DETD [0045] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.
- DETD [0047] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14 g of the HCN solution. The. . . .
- CLM What is claimed is:
- . . . 1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . . .
10. The use of a catalyst based on a ligand of structure II for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.
- IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenitrile 4635-87-4P  
 , 3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile  
 (phosphonite ligands and their use in hydrocyanation)
- IT 16529-56-9P, 2-Methyl-3-butenitrile 16529-66-1P,  
 trans-3-Pentenitrile  
 (phosphonite ligands and their use in hydrocyanation)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 (phosphonite ligands and their use in hydrocyanation)
- PI US 2003195372 A1 20031016 <--|  
 US 6737539 B2 20040518|
- SUMM [0002] The present invention concerns the use of catalyst compositions comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.
- SUMM [0003] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.
- SUMM [0004] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.
- SUMM [0005] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR1##

- SUMM [0007] The use of a catalyst based on a ligand of structure II for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.
- SUMM [0008] The present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR2##
- SUMM [0011] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure II I as described above and optionally a Lewis acid.
- SUMM [0012] Generally, a Group VII metal or a compound thereof is combined with at least one of the ligand structure II to provide the catalyst. Among the Group VII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by the ligand structure of the present invention is the most preferred source of Group VIII metal or Group VIII metal compound.
- SUMM [0013] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni(P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3).sub.3 and Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.2(C.sub.2H.sub.4), all of which are known in the art.
- SUMM [0014] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the ligand of structure II of the present invention in a ratio of nickel:bidentate ligand of 1:1. The ligand may be combined with nickel in a solvent, or preferably in the substrate medium. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions.
- SUMM [0016] The divalent nickel compound is combined with the ligand structure II of the present invention in a suitable solvent, preferably the unsaturated olefin, in a ratio of 1:1, or preferably at least 2:1. The combination is then combined with a suitable reducing agent at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.
- SUMM [0018] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a promoter. As used herein, the term "fluid" means gas, a liquid, or a

combination of these. Any fluid containing about 1 to 100% HCN can be used.

- SUMM [0019] A particularly significant use of the ligands of the present invention is in the hydrocyanation of olefins. In such a process, an olefinic compound such as a diolefinic compound can be converted to a nitrile or a dinitrile, or a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to form the mixture. However, it is preferred that HCN be added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the vessel. As an alternative, a cyanohydrin can be used as the source of HCN. See, for example, U.S. Pat. No. 3,655,723, incorporated herein by reference.
- SUMM [0020] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.
- SUMM [0021] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.
- SUMM [0023] The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in the gas phase.
- SUMM [0024] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to about 200° C. can be used with the range of 0° C. to 150° C. being preferred.
- SUMM [0031] The process of this invention can be carried out in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include, but are not limited to, ZnBr.sub.2, ZnI.sub.2, ZnCl.sub.2, ZnSO.sub.4, CuCl.sub.2, CuCl, Cu(O.sub.3SCF.sub.3).sub.2, CoCl.sub.2, CoI.sub.2, FeI.sub.2, FeCl.sub.3, FeCl.sub.2, FeCl.sub.2(THF).sub.2, TiCl.sub.2, TiCl.sub.4 (THF).sub.2, MnCl.sub.2, ScCl.sub.3, AlCl.sub.3, (C.sub.8H.sub.17)AlCl.sub.2, (C.sub.8H.sub.17).sub.2AlCl, (iso-C.sub.4H.sub.9).sub.2AlCl, Ph.sub.2AlCl, PhAlCl.sub.2, ReCl.sub.5, ZrCl.sub.4, NbCl.sub.5, VCl.sub.3, CrCl.sub.2, MoCl.sub.5, YCl.sub.3,

CdCl.sub.2, LaCl.sub.3, Er(O.sub.3SCF.sub.3).sub.3, Yb(O.sub.2CCF.sub.3).sub.3, SmCl.sub.3, B(C.sub.6H.sub.5).sub.3, TaCl.sub.5. Suitable promoters known in the art. These include metal salts, such as ZnCl.sub.2, CoI.sub.2, and SnCl.sub.2, and organometallic compounds (such as R.sub.8AlCl.sub.2, R.sub.8SnO.sub.3SCF.sub.3, and R.sub.8B, where R.sub.8 is an alkyl or aryl group). U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3, and (C.sub.6H.sub.5).sub.3Sn(CF.sub.3SO.sub.3), CH.sub.3SO.sub.3C.sub.6H.sub.5SO.sub.3, or (C.sub.6H.sub.5).sub.3BCN. The mole ratio of promoter to Group VIII metal present in the reaction can be within the range of about 1:16 to about 50:1.

SUMM [0038] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitrites. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees C. to 150 degrees C., and preferably from 80 degrees C. to 120 degrees C. A solvent may be used. Examples of a suitable solvent include but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitrites such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof.

DETD [0039] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.

DETD [0040] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1:1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1:1:1. The molar ratio of trans-3PN to Ni was 200 equivalents. The reaction vessel was heated to the temperature as described in the following Tables and hydrogen cyanide was delivered by slow evaporation of the hydrogen cyanide from a reservoir connected to the reaction vessel by a feed tube in an otherwise closed reaction system. The reaction was analyzed after 15 hours. The reaction mixture was analyzed using standard Gas Chromatograph methodology. Tables I-through III list the conversion of pentenenitriles to dinitriles and the selectivity to adiponitrile, defined as the ratio of adiponitrile over all dinitriles, in this hydrocyanation reaction.

TABLE I

Promoter: ZnCl.sub.2		
Conversion to	ligand	Selectivity to
Dinitrile		ADN

50° C.

Example 1	##STR6##	
73.8		91.0

Example 2	##STR7##	
2.2		81.8

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Example 3      ##STR8##  
57.4                      90.6

Example 4      ##STR9##  
32.7                      87.6

Example 5      ##STR10##  
87.5                      88.7

Example 6      ##STR11##  
28.2                      85.1

80° C.

Example 7      ##STR12##  
13.5                      82.9

Example 8      ##STR13##  
58.8                      73.0

Example 9      ##STR14##  
66.0                      77.2

Example 10     ##STR15##  
83.2                      73.7

DETD [0045] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.

DETD [0047] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14 g of the HCN solution. The vessel was sealed and placed in a reactor set at 100° C. Samples were removed after three hours.

1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR28## wherein the X groups are either the same or different unbridged organic aromatic groups as described in Formula I, wherein Q is a substituted or unsubstituted divalent aromatic or non aromatic hydrocarbon radical. The substituent on the Q groups is independently selected from the group consisting of C1 to C12 alkyl, cycloalkyl, alkoxy, alkylaryl, aryl, hetero aryl, cyano

10. The use of a catalyst based on a ligand of structure II for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenitrile 4635-87-4P  
, 3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile  
(phosphonite ligands and their use in hydrocyanation)

IT 16529-56-9P, 2-Methyl-3-butenitrile 16529-66-1P,  
trans-3-Pentenitrile  
(phosphonite ligands and their use in hydrocyanation)

IT 74-90-8, Hydrogen cyanide, reactions 166-99-0,  
1,3-Butadiene, reactions  
(phosphonite ligands and their use in hydrocyanation)

IT 4635-87-4P, 3-Pentenitrile 16545-78-1P,  
cis-3-Pentenitrile  
(phosphonite ligands and their use in hydrocyanation)



10/586490

RN 4635-87-4 USPATFULL  
CN 3-Pentenitrile (CA INDEX NAME)



RN 16545-78-1 USPATFULL  
CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 16529-66-1P, trans-3-Pentenitrile  
(phosphonite ligands and their use in hydrocyanation)  
RN 16529-66-1 USPATFULL  
CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

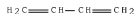
Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
(phosphonite ligands and their use in hydrocyanation)  
RN 74-90-8 USPATFULL  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL  
CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 50 OF 60 USPATFULL on STN  
ACCESSION NUMBER: 2003:277344 USPATFULL Full-text  
TITLE: PHOSPHONITE LIGANDS AND THEIR USE IN HYDROCYANATION

INVENTOR(S): Lenges, Christian P., Wilmington, DE, UNITED STATES  
 Ritter, Joachim C., Wilmington, DE, UNITED STATES

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2003195371	A1	20031016	<--
	US 6660877	B2	20031209	
APPLICATION INFO.:	US 2002-93655	A1	20020307	(10)
DOCUMENT TYPE:	Utility			
FILE SEGMENT:	APPLICATION			
LEGAL REPRESENTATIVE:	E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805			
NUMBER OF CLAIMS:	10			
EXEMPLARY CLAIM:	1			
LINE COUNT:	444			
CAS INDEXING IS AVAILABLE FOR THIS PATENT.				

AB Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM [0001] The present invention concerns the use of catalyst compositions comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.

SUMM [0002] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.

SUMM [0003] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.

SUMM [0004] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . .

SUMM [0008] The use of a catalyst based on a ligand of structures I, II and III for the hydrocyanation and/or the positional isomerization or double bond. . .

SUMM . . . present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR4##

SUMM [0014] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure I, II or. . .

- SUMM . . . a compound thereof is combined with at least one of the ligand structures I, II or III to provide the catalyst. Among the Group VIII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by. . .
- SUMM [0016] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni(P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3).sub.3. . .
- SUMM [0017] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the. . . of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or. . .
- SUMM . . . at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.
- SUMM [0021] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a. . .
- SUMM . . . a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to. . .
- SUMM [0023] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the. . .
- SUMM [0024] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.
- SUMM . . . The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran. . .
- SUMM [0027] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to. . .
- SUMM . . . in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting. . . U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3, and

(C.sub.6H.sub.5).sub.3Sn(CF.sub.3SO.sub.3),  
CH.sub.3C.sub.6H.sub.5SO.sub.3, or (C.sub.6H.sub.5).sub.3BCN. The mole  
ratio of promoter to Group. . .

SUMM [0041] The catalyst compositions of the present invention may also be  
used in the isomerization of allylic nitrites. The catalyst  
composition is combined with the allylic nitrile in a vessel and the  
isomerization process is carried at from 0 degrees. . .

DETD [0042] The following non-limiting, representative examples illustrate  
the process and catalyst compositions of this invention. All parts,  
proportions, and percentages are by weight, unless otherwise indicated.  
In each example, the following. . .

DETD [0043] Catalyst solutions were prepared by mixing one of the bidentate  
ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1.1:1 and  
dissolving this in toluene. To the catalyst solution was added a  
solution of the promoter in the trans-3PN. The promoter: nickel molar  
ratio is 1.1:1. The molar. . .

DETD [0048] Catalyst Solution: For a typical multidentate phosphonite  
ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were  
combined in toluene to generate 3 g of catalyst solution.

DETD [0050] To a reaction vessel were added 0.1 ml of the catalyst  
solution. To this was added 0.18 g of the butadiene solution followed by  
0.14g of the HCN solution. The vessel. . .

CLM What is claimed is:  
. . . 1. A hydrocyanation process, said process comprising: contacting an  
ethylenically unsaturated olefin compound with HCN in the presence of a  
catalyst composition, wherein said catalyst composition comprises a  
Group VIII metal and a phosphonite ligand wherein the ligand having a  
structure selected from the group. . . .  
10. The use of a catalyst based on a ligand of structures I, II and  
III for the hydrocyanation and/or the positional isomerization or double  
bond. . .

IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenitrile 4635-87-4P  
, 3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile  
(phosphonite ligands and their use in hydrocyanation)

IT 16529-56-9P, 2-Methyl-3-butenitrile 16529-66-1P,  
trans-3-Pentenitrile  
(phosphonite ligands and their use in hydrocyanation)

IT 74-99-8, Hydrogen cyanide, reactions 106-99-0,  
1,3-Butadiene, reactions  
(phosphonite ligands and their use in hydrocyanation)

PI US 2003195371 A1 20031016 <--|  
US 6660877 B2 20031209|

SUMM [0001] The present invention concerns the use of catalyst compositions  
comprising a Group VIII metal and a multidentate phosphonite ligand for  
olefinic hydrocyanation and isomerization processes.

SUMM [0002] Certain phosphonites have been used as a part of hydrocyanation  
catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a  
catalyst composition in hydroformylation and hydrocyanation reactions.  
WO9843935 discloses the use of certain phosphonite ligands as part of a  
catalyst system in a process for producing an aldehyde. WO9946044  
relates to a hydroformylation process using phosphonite ligands as part  
of the catalyst system for hydroformylation reactions. U.S. Pat. No.  
6,242,633 discloses a process for the production of nitriles using  
catalysts containing phosphonite ligands. Further, WO9964155 discloses  
use of catalysts containing phosphorous ligands in hydrocyanation  
reactions.

SUMM [0003] Despite the disclosure of various ligands in hydrocyanation and  
hydroformylation processes. Catalyst compositions comprising certain

multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.

- SUMM [0004] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR1##
- SUMM [0008] The use of a catalyst based on a ligand of structures I, II and III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.
- SUMM [0009] The present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR4##
- SUMM [0014] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure I, II or III as described above and optionally a Lewis acid.
- SUMM [0015] Generally, a Group VIII metal or a compound thereof is combined with at least one of the ligand structures I, II or III to provide the catalyst. Among the Group VIII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by the ligand structure of the present invention is the most preferred source of Group VIII metal or Group VIII metal compound.
- SUMM [0016] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni(P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3).sub.3 and Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.2(C.sub.2H.sub.4), all of which are known in the art.
- SUMM [0017] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the ligand of structure I, II or III of the present invention in a ratio of nickel:bidentate ligand of 1:1. The ligand may be combined with nickel in a solvent, or preferably in the substrate medium. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions.
- SUMM [0019] The divalent nickel compound is combined with the ligand structure I, II or III of the present invention in a suitable solvent, preferably the unsaturated olefin, in a ratio of 1:1, or preferably at least 2:1. The combination is then combined with a suitable reducing agent at room temperature, or at a temperature that is appropriate for

the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.

SUMM [0021] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a promoter. As used herein, the term "fluid" means gas, a liquid, or a combination of these. Any fluid containing about 1 to 100% HCN can be used.

SUMM [0022] A particularly significant use of the ligands of the present invention is in the hydrocyanation of olefins. In such a process, an olefinic compound such as a diolefinic compound can be converted to a nitrile or a dinitrile, or a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to form the mixture. However, it is preferred that HCN be added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the vessel. As an alternative, a cyanohydrin can be used as the source of HCN. See, for example, U.S. Pat. No. 3,655,723, incorporated herein by reference.

SUMM [0023] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.

SUMM [0024] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.

SUMM [0026] The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitrites such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in the gas phase.

SUMM [0027] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to about 200° C. can be used with the range of 0° C. to 150° C. being preferred.

SUMM [0035] The process of this invention can be carried out in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an

inorganic or organometallic compound in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include, but are not limited to, ZnBr.sub.2, ZnI.sub.2, ZnCl.sub.2, ZnSO.sub.4, CuCl.sub.2, CuCl, Cu(O.sub.3SCF.sub.3).sub.2, CoCl.sub.2, CoI.sub.2, FeI.sub.2, FeCl.sub.3, FeCl.sub.2, FeCl.sub.2(THF).sub.2, TiCl.sub.2, TiCl.sub.4 (THF).sub.2, MnCl.sub.2, ScCl.sub.3, AlCl.sub.3, (C.sub.8H.sub.17)AlCl.sub.2, (C.sub.8H.sub.17).sub.2AlCl, (iso-C.sub.4H.sub.9).sub.2AlCl, Ph.sub.2AlCl, PhAlCl.sub.2, ReCl.sub.5, ZrCl.sub.4, NbCl.sub.5, VCl.sub.3, CrCl.sub.2, MoCl.sub.5, YCl.sub.3, CdCl.sub.2, LaCl.sub.3, Er(O.sub.3SCF.sub.3).sub.3, Yb(O.sub.2CCF.sub.3).sub.3, SmCl.sub.3, B(C.sub.6H.sub.5).sub.3, TaCl.sub.5. Suitable promoters known in the art. These include metal salts, such as ZnCl.sub.2, CoI.sub.2, and SnCl.sub.2, and organometallic compounds (such as R.sub.8AlCl.sub.2, R.sub.8SnO.sub.3SCF.sub.3, and R.sub.8B, where R.sub.8 is an alkyl or aryl group). U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3, and (C.sub.6H.sub.5).sub.3Sn(CF.sub.3SO.sub.3), CH.sub.3C.sub.6H.sub.5SO.sub.3, or (C.sub.6H.sub.5).sub.3BCN. The mole ratio of promoter to Group VIII metal present in the reaction can be within the range of about 1:16 to about 50:1.

- SUMM [0041] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitriles. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees C. to 150 degrees C., and preferably from 80 degrees C. to 120 degrees C. A solvent may be used. Examples of a suitable solvent include but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof.
- DETD [0042] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.
- DETD [0043] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1.1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1.1:1. The molar ratio of trans-3PN to Ni was 200 equivalents. The reaction vessel was heated to the temperature as described in the following Tables and hydrogen cyanide was delivered by slow evaporation of the hydrogen cyanide from a reservoir connected to the reaction vessel by a feed tube in an otherwise closed reaction system. The reaction was analyzed after 15 hours. The reaction mixture was analyzed using standard Gas Chromatograph methodology. Tables I-through III list the conversion of pentenenitriles to dinitriles and the selectivity to adiponitrile, defined as the ratio of adiponitrile over all dinitriles, in this hydrocyanation reaction.

TABLE I

Promoter: ZnCl.sub.2  
Conversion to      Selectivity to

	ligand	
Dinitrile	ADN	
50° C.		
Example 1	##STR11##	
73.8		91.0
Example 2	##STR12##	
2.2		81.8
Example 3	##STR13##	
57.4		90.6
Example 4	##STR14##	
32.7		87.6
Example 5	##STR15##	
87.5		88.7
Example 6	##STR16##	
28.2		85.1

80° C.

Example 7	##STR17##	
13.5		82.9
Example 8	##STR18##	
58.8		73.0
Example 9	##STR19##	
66.0		77.2
Example 10	##STR20##	
83.2		73.7

DETD [0048] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.

DETD [0050] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14g of the HCN solution. The vessel was sealed and placed in a reactor set at 100° C. Samples were removed after three hours.

1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR33## wherein the X groups can be independently chosen to be either a substituted or unsubstituted organic aromatic group. The substituent on the X groups is independently selected from the group consisting of C1 to C12 alkyl, perfluoroalkyl, cycloalkyl, alkoxy, acetal, ketal, alkylaryl, aryl, hetero aryl, cyano, and hydrogen. ##STR34## wherein the X groups are either the same or different unbridged organic aromatic groups as described in Formula I, wherein Q is a substituted or unsubstituted divalent aromatic or non aromatic hydrocarbon radical. The 25 substituent on the Q groups is independently selected from the group consisting of C1 to C12 alkyl, cycloalkyl, alkoxy, alkylaryl, aryl, hetero aryl, cyano ##STR35## wherein X and Q are as described in Formula II, and L is a linking group selected from the group consisting



of -CR1 R2-, --O--, --S--, --CO-- (wherein each of R1-R2 are independent of one another, are a hydrogen atom, a C1-12 alkyl group, or an aryl group), and each of m and m' which are independent of each other, are 0 or 1.

10. The use of a catalyst based on a ligand of structures I, II and III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

- IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenitrile 4635-87-4P  
 , 3-Pentenitrile 16545-78-1P, cis-3-Pentenitrile  
 (phosphonite ligands and their use in hydrocyanation)  
 IT 16529-56-9P, 2-Methyl-3-butenitrile 16529-66-1P,  
 trans-3-Pentenitrile  
 (phosphonite ligands and their use in hydrocyanation)  
 IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 (phosphonite ligands and their use in hydrocyanation)  
 IT 4635-87-4P, 3-Pentenitrile 16545-78-1P,  
 cis-3-Pentenitrile  
 (phosphonite ligands and their use in hydrocyanation)  
 RN 4635-87-4 USPATFULL  
 CN 3-Pentenitrile (CA INDEX NAME)



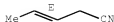
- RN 16545-78-1 USPATFULL  
 CN 3-Pentenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



- IT 16529-66-1P, trans-3-Pentenitrile  
 (phosphonite ligands and their use in hydrocyanation)  
 RN 16529-66-1 USPATFULL  
 CN 3-Pentenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
 1,3-Butadiene, reactions  
 (phosphonite ligands and their use in hydrocyanation)  
 RN 74-90-8 USPATFULL  
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL  
CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 51 OF 60 USPATFULL on STN  
ACCESSION NUMBER: 2003:220400 USPATFULL Full-text  
TITLE: Supported bis(phosphorus) ligands and their use in the catalysis  
INVENTOR(S): Cobb, Michael W., Wilmington, DE, UNITED STATES  
Qiu, Weiming, Wilmington, DE, UNITED STATES

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 2003153691	A1	20030814
	US 6984604	B2	20060110
APPLICATION INFO.:	US 2002-305230	A1	20021126 (10)

	NUMBER	DATE
PRIORITY INFORMATION:	US 2001-333365P	20011126 (60)
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805	
NUMBER OF CLAIMS:	26	
EXEMPLARY CLAIM:	1	
LINE COUNT:	1383	

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Supported bis(phosphorus) ligands are disclosed for use in a variety of catalytic processes, including the isomerization, hydrogenation, hydroformylation, and hydrocyanation of unsaturated organic compounds. Catalysts are formed when the ligands are combined with a catalytically active metal, such as nickel.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . The group X may contain from 1 to 50 carbon atoms. It may also optionally contain heteroatoms such as oxygen, nitrogen, halogen, and the like, and also functional groups such as ethers, alcohols, esters, amides, as well as others. The groups. . .

SUMM [0085] A non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used.

SUMM . . . unsaturated organic compound can also be substituted with one

or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile, . . .

SUMM . . . phase. A given catalyst is loaded into a reactor, such as a tubular reactor, taking care to avoid exposure of air-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and. . .

DETD . . . above nickel catalyst, 19 mg of zinc chloride and 5 mL of 3-pentenitrile. The hydrocyanation reaction was done at a nitrogen flow rate of 12 cc/min with the oil bath at 50° C. for 180 minutes and then 70° C. for. . .

IT 74-90-8, Hydrocyanic acid, reactions 106-99-0, Butadiene, reactions 630-08-0, Carbon monoxide, reactions 4635-87-4, 3-Pentenitrile 16529-56-9, 2-Methyl-3-butenitrile

(polymer supported bis(phosphorus)ligands and their use in catalysis)  
SUMM [0067] Polymer-supported bis(phosphorus) ligands have been prepared by a variety of methods known in the art, for example, see descriptions in WO 93,03839; U.S. Pat. No. 4,769,498 and U.S. Pat. No. 4,668,651. In general, the transformation involves the reaction of a phosphorus halide, typically but not limited to chloride, with the diol to form P-O bonds. The phosphorus halide may be any compound of the type  $PY_{sub.n}X_{sub.3-n}$ , where Y=halide, X=alkoxide, aryloxy, alkyl, aryl, and n=3, 2, or 1. The preferred phosphorus halides of the present invention are those where Y=Cl; X=alkoxide, aryloxy, alkyl, or aryl; and n=1. The group X may contain from 1 to 50 carbon atoms. It may also optionally contain heteroatoms such as oxygen, nitrogen, halogen, and the like, and also functional groups such as ethers, alcohols, esters, amides, as well as others. The groups X may or may not be linked to form a cyclic structure. The  $PX_{sub.2}$  moiety may form a ring and X may also be alkoxide, aryloxy, alkyl, aryl, or a combination of them. Many dialkyl chlorophosphines and diaryl chlorophosphines are commercially available, or may be prepared by methods known in the art, for example, J. Am. Chem. Soc. 1994, 116, 9869. Phosphorochloridites, may be prepared by a variety of methods known in the art, for example, see descriptions in Polymer 1992, 33,161; Inorg. Syn. 1966, 8, 68; U.S. Pat. No. 5,210,260; Z. Anorg. Allg. Chem. 1986, 535, 221. For example, the reaction of 2,2'-biphenol with phosphorus trichloride gives 1,1'-biphenyl-2,2'-diylphosphorochloridite.

SUMM [0085] A non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used.

SUMM [0094] The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, 7-octen-1-ol, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol, 3-pentenal, 4-pentenal, and combinations of two or more thereof.

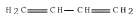
SUMM [0104] The hydroformylation process can be run in solution or in the gas phase. When the hydroformylation is carried out in the vapor phase, the preferred temperature range is from about 50° C. to about 180° C., most preferably from about 90° C. to 110° C. The temperature must be chosen so as to maintain all of the reactants and products in the vapor phase, but low enough to prevent deterioration of the catalyst. The particular preferred temperature depends to some extent on the catalyst being used, the olefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical and can be from about 0.101 to 1.01 MPa. The pressure and temperature combination must be chosen so as to maintain reactants and products in the vapor phase. A given catalyst is loaded into a reactor, such as a tubular reactor, taking care to avoid exposure of air-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and are conveniently recovered by cooling. The reactor effluent can be directly connected to a sampling valve and can be analyzed by gas chromatography. Aldehydic products, such as linear and branched butyraldehydes obtained from hydroformylation of propylene, can be quantitatively separated and analyzed using a 30 M DB-Wax® capillary GC column.

DETD [0179] A three necked flask was charged with 0.284 g of the above nickel catalyst, 19 mg of zinc chloride and 5 mL of 3-pentenitrile. The hydrocyanation reaction was done at a nitrogen flow rate of 12 cc/min with the oil bath at 50° C. for 180 minutes and then 70° C. for 120 minutes. GC analysis indicated 87% of the pentenenitriles have converted to dinitriles with an adiponitrile distribution of 93%.

IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,  
Butadiene, reactions 630-08-0, Carbon monoxide, reactions  
4635-87-4, 3-Pentenitrile 16529-56-9, 2-Methyl-3-  
butenenitrile  
(polymer supported bis(phosphorus)ligands and their use in catalysis)  
IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,  
Butadiene, reactions 4635-87-4, 3-Pentenitrile  
(polymer supported bis(phosphorus)ligands and their use in catalysis)  
RN 74-90-8 USPATFULL  
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL  
CN 1,3-Butadiene (CA INDEX NAME)



RN 4635-87-4 USPATFULL



L88 ANSWER 52 OF 60 USPATFULL on STN

ACCESSION NUMBER: 2003:208079 USPATFULL Full-text

TITLE: Phosphorus-containing compositions and their use in hydrocyanation, isomerization and hydroformylation reactions

INVENTOR(S): Gagne, Michel R., Carrboro, NC, UNITED STATES  
 Moloy, Kenneth G., Hockessin, DE, UNITED STATES  
 Radu, Nora S., Landenberg, PA, UNITED STATES  
 Santora, Brian P., River Falls, WI, UNITED STATES  
 Tam, Wilson, Boothwyn, PA, UNITED STATES

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 2003144440	A1	20030731
	US 6660876	B2	20031209
APPLICATION INFO.:	US 2001-994135	A1	20011126 (9)
DOCUMENT TYPE:	Utility		
FILE SEGMENT:	APPLICATION		
LEGAL REPRESENTATIVE:	E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805		
NUMBER OF CLAIMS:	45		
EXEMPLARY CLAIM:	1		
LINE COUNT:	2482		

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A polymeric, phosphorus-containing composition made by heating, in the presence of an initiator, preferably a free radical initiator, and optionally in the presence of one or more comonomers, at least one substituted phosphonylated 2,2'-dihydroxyl-1,1'-binaphthalene or at least one substituted 2,2'-dihydroxyl-1,1'-biphenylene.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

DETD . . . unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted, ethylenically unsaturated, organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile, . . .

DETD . . . into a reactor, such as a tubular reactor, taking care to avoid exposure of oxygen-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and. . .

DETD . . . herein, a non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used, if desired, at the expense of loss of a proportion of the catalyst activity through oxidation. Impurities. . .

- DETD . . . in a thermostatically controlled oil bath. HCN was delivered to the flask as an HCN/N.sub.2 gas mixture by bubbling dry nitrogen carrier gas through liquid HCN maintained in an ice bath at 0° C. This provided a vapor stream that was about 35% by volume HCN. The rate of nitrogen gas flow determined the rate of HCN delivery. Samples were periodically analyzed by gas chromatography (GC).
- DETD [0158] Aspect 2: Preparation of ethylenically unsaturated, phosphorus-containing bidentate ligand (1): Under nitrogen atmosphere, a 100 mL flask with magnetic stir bar was charged with 2.450 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.865 grams of acryloyl. . .
- DETD [0203] Aspect 2: Preparation of ethylenically unsaturated ligand (8): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 1.880 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.664 grams of acryloyl chloride. . .
- DETD . . . and 5 mL of 3PN in a closed reactor was placed in a 50° C. oil bath and HCN saturated nitrogen was delivered at a nitrogen flow rate of 24 cc/min. The reaction was heated at 50° C. for 1 hour and then at 70° C. for 30 minutes. Nitrogen flow was decreased to 12 cc/min. and the reaction was run at 70° C. for an additional 90 minutes. The. . .
- DETD [0227] Aspect 2: Preparation of ethylenically unsaturated ligand (12): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 0.931 grams of the monoacrylate of 2,2-bis(4-hydroxy-3-methylphenyl)propane (prepared from. . .
- DETD . . . to the mixture. The mixture was heated in a 50° C. oil bath and HCN was delivered with 24 cc/min. nitrogen flow rate. After 90 minutes of reaction, GC analysis indicated 57.6% conversion of 3PN with 92% selectivity to ADN. To. . . but the reaction was allowed to continue at 50° C. for 120 minutes. The mixture was allowed to sit under nitrogen at room temperature overnight. GC analysis indicated 62% conversion of 3PN with 91.3% selectivity to ADN.
- DETD . . . begin an additional reaction. The reaction was placed in a 70° C. oil bath and HCN was delivered with a nitrogen flow rate of 30 cc/min. The reaction was then stored at room temperature overnight. The mixture was then heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 30 minutes. GC analysis indicated 75% conversion of 3PN with selectivity to ADN of. . . was added 5 mL of 3PN. The mixture was heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 210 minutes. GC analysis indicated 65% conversion of 3PN with selectivity to ADN of. . .
- DETD [0243] Aspect 2: Preparation of the diphosphite ligand (13): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.2O (5 mL) solution of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.051 g, 1.5x10.sup.-4 mol) and Et.sub.3N (0.040, 3.9x10.sup.-4 mol) was. . .
- DETD [0244] Aspect 3: Polymerization of the ethylenically unsaturated compound (13) with divinylbenzene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.027 g, 2.7x10.sup.-5 mol) described in. . .
- DETD [0247] Aspect 2: Preparation of ethylenically unsaturated diphosphite ligand (14): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.2O (5 mL) solution of 3,3',4,4',5,5',6,6'-octamethyl-2,2'-dihydroxy-1,1'-biphenyl (0.100 g, 0.67 mmol) and Et.sub.3N (0.152 g, 1.5 mmol). . .
- DETD [0248] Aspect 3: Polymerization of the ethylenically unsaturated compound (14) with divinylbenzene and styrene: Under an atmosphere of

- nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.100 g, 0.09 mmol) described in. . .
- DETD [0251] Aspect 5.1: Polymerization of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl with styrene: Under nitrogen atmosphere, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.500g, 1.48 mmol), AIBN (0.040 g),. . .
- DETD [0252] Aspect 5.2: Formation of the diphosphite ligand from the polymeric precursor of Example 15: Under nitrogen atmosphere, a cold solution (-30° C.) of o-cresol (0.027 g, 0.25 mmol) in toluene (5 mL) was added to a. . .
- DETD . . . mL of 3PN. The mixture was heated in a 70 C. oil bath and HCN was delivered with 12 cc/min. nitrogen flow rate. After 180 minutes, GC indicated 93.9% conversion to dinitrile with ADN selectivity of 88.4%.
- IT 106-99-6, Butadiene, reactions 4635-87-4, 3-Pentenitrile  
(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns. and their use in hydrocyanation, isomerization and hydroformylation reactions)
- IT 74-85-1, Ethylene, reactions 74-96-8, Hydrogen cyanide, reactions 79-97-0, 2,2-Bis(4-hydroxy-3-methylphenyl)propane 814-68-6, Acryloyl chloride 7719-12-2, Phosphorus trichloride 13185-00-7, 6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthyl 26567-10-2 31860-10-3 50291-18-4 100930-72-1 532941-08-5 538345-81-2 538346-27-9 538346-36-0  
(manufacture of unsatd. phosphorus-containing compns. and their use in hydrocyanation, isomerization and hydroformylation reactions)
- DETD [0135] The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted, ethylenically unsaturated, organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, 7-octen-1-al, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol, 3-pentenal, 4-pentenal, and combinations of two or more thereof.
- DETD [0144] The hydroformylation process can be run in solution or in the gas phase. When the hydroformylation is carried out in the vapor phase, the preferred temperature range is from about 50° C. to about 180° C., most preferably from about 90° C. to 110° C. The temperature must be chosen high enough so as to maintain all of the reactants and products in the vapor phase, but low enough to prevent deterioration of the catalyst. The particular preferred temperature depends to some extent on the catalyst being used, the olefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical and can be from about 0.1 to 1.0 MPa. The pressure and temperature combination must be chosen so as to maintain reactants and products in the vapor phase. A given catalyst is loaded into a reactor, such as a tubular reactor, taking care to avoid exposure of oxygen-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and are conveniently recovered by cooling. The reactor effluent can be directly

connected to a sampling valve and can be analyzed by gas chromatography. Aldehydic products, such as linear and branched butyraldehydes obtained from hydroformylation of propylene, can be quantitatively separated and analyzed using a 30M DB-Wax® capillary GC column.

DETD [0145] For the hydrocyanation, isomerization, and hydroformylation processes described herein, a non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used, if desired, at the expense of loss of a proportion of the catalyst activity through oxidation. Impurities that are detrimental to the catalyst should be kept to a minimum.

DETD [0156] Hydrocyanation of 3-pentenitrile was also performed by slowly adding the HCN to the reaction mixture. The catalyst composition and 3-pentenitrile were heated in a thermostatically controlled oil bath. HCN was delivered to the flask as an HCN/N.sub.2 gas mixture by bubbling dry nitrogen carrier gas through liquid HCN maintained in an ice bath at 0° C. This provided a vapor stream that was about 35% by volume HCN. The rate of nitrogen gas flow determined the rate of HCN delivery. Samples were periodically analyzed by gas chromatography (GC).

DETD [0158] Aspect 2: Preparation of ethylenically unsaturated, phosphorus-containing bidentate ligand (1): Under nitrogen atmosphere, a 100 mL flask with magnetic stir bar was charged with 2.450 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.865 grams of acryloyl chloride, 40 mL of toluene and 8 mL of THF. The mixture was cooled to -30° C. and 1.2 grams of triethylamine in 15 mL of toluene was added. About a quarter of the solvent was removed under vacuum and the mixture cooled to -30° C. To this mixture was added 2.266 grams of the phosphorodichlorodite of 2-isopropylphenol and 1.2 grams of triethylamine in 10 mL of toluene. The mixture was stirred for one and one-half hours and cooled to -30° C. To the mixture was added 1.157 grams of 3,3',5,5'-tetramethyl-2,2'-biphenol and 1.2 grams of triethylamine. The mixture was kept at -30° C. overnight and then filtered. Solvent was removed to give 5.978 grams of a tacky brown solid (.sup.31P NMR in CDCl.sub.3: 142.21, 142.15, 135.20, 135.11, 134.74, 134.29, 132.01, 131.96, and 131.13).

DETD [0203] Aspect 2: Preparation of ethylenically unsaturated ligand (8): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 1.880 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.664 grams of acryloyl chloride, and 40 mL of THF. The mixture was cooled to -30° C. and a pre-cooled solution (at -30° C.) containing 1 gram of triethylamine in 15 mL of THF was added. The THF was removed under vacuum and the residue dissolved in 50 mL of THF. To this slurry was added 0.503 grams of phosphorus trichloride. The mixture was cooled to -30° C. and a pre-cooled solution containing 0.5 gram of triethylamine in 10 mL of THF was added. After stirring for several days, 0.598 grams of 3,3'-diisopropyl-5,5',6,6'-tetramethyl-2,2'-biphenol was added along with 1.2 grams of triethylamine. The mixture was stirred for forty minutes, filtered and the solvent was removed under vacuum to give 3.146 grams of a yellow solid (.sup.31P NMR (CDCl.sub.3): 135.58, 135.25, 135.18, 134.80, 134.71, 132.71, 131.90, 130.80, 127.94, and 127.87).

DETD [0226] Aspect 10: Semibatch 3-pentenitrile hydrocyanation using nickel catalyst: A reaction mixture of 0.567 grams of the above catalyst, 0.027 grams of zinc chloride, 5 mL of toluene and 5 mL of 3PN in a closed reactor was placed in a 50° C. oil bath and HCN saturated nitrogen was delivered at a nitrogen flow rate of 24 cc/min. The reaction was heated at 50° C. for 1 hour and then at 70° C. for 30 minutes. Nitrogen flow was decreased to 12 cc/min. and the reaction was run at 70° C. for an additional 90 minutes. The



temperature was then increased to 80° C. and the reaction was continued for another 90 minutes. GC analysis indicated 68% conversion of 3-pentenitrile to dinitrile with an ADN selectivity of 89%.

DETD [0227] Aspect 2: Preparation of ethylenically unsaturated ligand (12): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 0.931 grams of the monoacrylate of 2,2-bis(4-hydroxy-3-methylphenyl)propane (prepared from the reaction of acryloyl chloride with 2,2-bis(4-hydroxy-3-methylphenyl)propane), 0.627 grams of the phosphorodichloridite of o-cresol, and 40 mL of toluene. The mixture was cooled to -30° C. and a precooled solution (at -30° C.) containing 0.4 grams of triethylamine in 15 mL of toluene was added. After stirring for 2 hours, .sup.31P NMR in CDCl.sub.3 indicated a peak at 162.8 ppm. The mixture was cooled to -30° C. and 0.448 grams of 3,3',4,4',5,5'-hexamethyl-2,2'-biphenol and 0.65 grams of triethylamine in 2 mL of THF were added. After stirring overnight, the mixture was filtered and the THF removed under vacuum to give a yellow solid. The solid was dissolved in 10 mL of toluene and 0.8 grams of triethylamine was added in 5 mL of THF. The mixture was stirred overnight and filtered. The solvent was removed. .sup.31P NMR indicated some phosphorodichloridite still present. The residue was dissolved in THF and 0.75 grams of triethylamine were added. After stirring overnight, the mixture was filtered through silica gel, and the solvent was removed under vacuum. 1.225 Grams of yellow solid were recovered (.sup.31P NMR in CDCl.sub.3: 137.47, 137.31, 135.29, 135.21, 135.15, 135.00, 134.82, 134.73, 134.40, 134.31, 133.41, 133.40, 132.07, 131.98, 130.44, 127.74, and 127.69).

DETD [0235] Aspect 10: Hydrocyanation of 3-pentenitrile: 29 milligrams of ZnCl.sub.2 and 5 mL of 3PN were added to the mixture. The mixture was heated in a 50° C. oil bath and HCN was delivered with 24 cc/min. nitrogen flow rate. After 90 minutes of reaction, GC analysis indicated 57.6% conversion of 3PN with 92% selectivity to ADN. To the mixture was added 5 mL of 3PN and the reaction was continued for 90 minutes. At this point, HCN delivery was stopped but the reaction was allowed to continue at 50° C. for 120 minutes. The mixture was allowed to sit under nitrogen at room temperature overnight. GC analysis indicated 62% conversion of 3PN with 91.3% selectivity to ADN.

DETD [0236] Ligand recycle: At this time, the solvent was removed via syringe from the reactor. 5 mL of toluene, 5 mL of 3PN and 29 milligrams of ZnCl.sub.2 were added to begin an additional reaction. The reaction was placed in a 70° C. oil bath and HCN was delivered with a nitrogen flow rate of 30 cc/min. The reaction was then stored at room temperature overnight. The mixture was then heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 30 minutes. GC analysis indicated 75% conversion of 3PN with selectivity to ADN of 92.2%. To this mixture was added 5 mL of 3PN. The mixture was heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 210 minutes. GC analysis indicated 65% conversion of 3PN with selectivity to ADN of 91.8%.

DETD [0243] Aspect 2: Preparation of the diphosphite ligand (13): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.2O (5 mL) solution of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.051 g, 1.5x10.sup.-4 mol) and Et.sub.3N (0.040, 3.9x10.sup.-4 mol) was slowly added to a Et.sub.2O (5 mL) solution of phosphorochlorodite of 2-isopropoxyphenol (0.140 g, 3.9x10.sup.-4 mol). The solution was allowed to warm up to room temperature and was stirred for one hour. The reaction mixture was filtered through celite and alumina. The volatiles were evaporated to yield a white powder in 67% yield. (0.100 g).

DETD [0244] Aspect 3: Polymerization of the ethylenically unsaturated

compound (13) with divinylbenzene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.027 g, 2.7x10<sup>-5</sup> mol) described in example 13, AIBN (0.002 g), DVB (0.1900 g) and THF (0.184 g). This vial was screwed shut and placed in a 70° C. oil bath for 24 hours.

After polymerization, the polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (0.350 g) was insoluble in all organic solvents. Elemental analysis: P found: 1.51%.

DETD [0247] Aspect 2: Preparation of ethylenically unsaturated diphosphite ligand (14): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.2O (5 mL) solution of 3,3',4,4',5,5',6,6'-octamethyl-2,2'-dihydroxy-1,1'-biphenyl (0.100 g, 0.67 mmol) and Et.sub.3N (0.152 g, 1.5 mmol) was slowly added to an Et.sub.2O (5 mL) solution of phosphorochlorodite of trans-2-ethoxy-5-(1-propenyl)phenol (0.631 g, 1.5 mmol). The solution was allowed to warm to room temperature and was stirred for one hour. The reaction mixture was filtered through celite and alumina. The volatiles were evaporated to give 86% yield of a white powder (0.623 g).

DETD [0248] Aspect 3: Polymerization of the ethylenically unsaturated compound (14) with divinylbenzene and styrene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.100 g, 0.09 mmol) described in example 14, AIBN (0.005 g), DVB (0.40 g), styrene (0.70 g) and THF (1.5 mL). This vial was screwed shut and placed in a 70° C. oil bath for 48 hours, after which DVB (0.75 g) and AIBN (0.005 g) were added and the vial was returned to the oil bath. After 48 hours, the opaque polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (0.137 g) was insoluble in all organic solvents.

DETD [0251] Aspect 5.1: Polymerization of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl with styrene: Under nitrogen atmosphere, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.500g, 1.48 mmol), AIBN (0.040 g), styrene (4.0 mL) and THF (4.0 mL). The vial was screwed shut and placed in a 70° C. oil bath for 24 hours. After polymerization, the polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (4.8 g) was insoluble in all organic solvents.

DETD [0252] Aspect 5.2: Formation of the diphosphite ligand from the polymeric precursor of Example 15: Under nitrogen atmosphere, a cold solution (-30° C.) of o-cresol (0.027 g, 0.25 mmol) in toluene (5 mL) was added to a solution of the phosphorodichlorodite of phenol (0.045 g, 0.25 mmol) and n-Bu.sub.3N (0.047 g, 0.25 mmol) in toluene (5 mL). The resulting mixture was allowed to stir at room temperature for 1.5 hours, after which it was cooled to -30° C. This cold solution was added to a cold slurry of polymer from example 15 (0.328 g, 0.10 mmol) and n-Bu.sub.3N (0.047 g, 0.25 mmol) in toluene (5 mL). This mixture was stirred at room temperature for five hours. The polymer product was isolated by filtration and washed with toluene and acetonitrile. After drying under vacuum, a tacky solid (0.350 g) was obtained.

DETD [0265] Aspect 10: Semi-batch hydrocyanation of 3-pentenitrile: To 0.388 g of the catalyst from Example 18B was added 19 mg of zinc chloride and 5 mL of 3PN. The mixture was heated in a 70° C. oil bath and HCN was delivered with 12 cc/min. nitrogen flow rate. After 180 minutes, GC indicated 93.9% conversion to dinitrile with ADN selectivity of 88.4%.

IT 106-39-0, Butadiene, reactions 4635-87-4,  
3-Pentenitrile

(hydrocyanation of; manufacture of unsatd. phosphorus-containing comps. and their use in hydrocyanation, isomerization and hydroformylation reactions)

IT 74-85-1, Ethylene, reactions 74-90-8, Hydrogen cyanide, reactions 79-97-0, 2,2-Bis(4-hydroxy-3-methylphenyl)propane 814-68-6, Acryloyl chloride 7719-12-2, Phosphorus trichloride 13185-00-7, 6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthyl 26567-10-2 31860-10-3 50291-18-4 100930-72-1 532941-08-5 538345-81-2 538346-27-9 538346-36-0

(manufacture of unsatd. phosphorus-containing comps. and their use in hydrocyanation, isomerization and hydroformylation reactions)

IT 106-99-0, Butadiene, reactions 4635-87-4, 3-Pentenitrile

(hydrocyanation of; manufacture of unsatd. phosphorus-containing comps. and their use in hydrocyanation, isomerization and hydroformylation reactions)

RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



RN 4635-87-4 USPATFULL

CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions

(manufacture of unsatd. phosphorus-containing comps. and their use in hydrocyanation, isomerization and hydroformylation reactions)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 53 OF 60 USPATFULL on STN

ACCESSION NUMBER: 2003:65616 USPATFULL Full-text

TITLE: Copper-catalyzed vapor phase hydrocyanation of diolefinic compounds

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	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 2003045740	A1	20030306	<--
	US 6753440	B2	20040622	
APPLICATION INFO.:	US 2002-140736	A1	20020508	(10)

	NUMBER	DATE
PRIORITY INFORMATION:	US 2001-290294P	20010511 (60)
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805	
NUMBER OF CLAIMS:	18	
EXEMPLARY CLAIM:	1	
LINE COUNT:	496	

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A catalyzed vapor phase process for the hydrocyanation of acyclic diolefinic compounds to olefinic nitriles is described in which the olefinic double bond is not conjugated to the triple bond of the cyano group, wherein a catalyst composition comprising supported copper salts is used.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Copper-catalyzed vapor phase hydrocyanation of diolefinic compounds

AB A catalyzed vapor phase process for the hydrocyanation of acyclic diolefinic compounds to olefinic nitriles is described in which the olefinic double bond is not conjugated to the triple bond of the cyano group, wherein a catalyst composition comprising supported copper salts is used.

SUMM . . . the invention relates to a gas phase process for the hydrocyanation of diolefinic compounds to produce nonconjugated acyclic nitriles utilizing catalyst compositions comprising copper salts, dispersed on supports, including carbon, silica, alumina and a variety of metal oxides.

SUMM [0003] Catalytic hydrocyanation systems, particularly pertaining to the hydrocyanation of olefins, are known in the art. For example, liquid phase systems useful. . .

SUMM . . . the liquid phase, with all attendant waste disposal problems. For example, U.S. Pat. No. 4,240,976 utilized copper halide as a catalyst; U.S. Pat. No. 4,230,634 utilized copper inorganic salts in the presence of organic nitriles; and U.K. Patent No. 2,077,260 used. . further hydrocyanated. For example, U.S. Pat. No. 3,584,029 teaches that propionitrile is prepared by reaction of HCN with ethylene over catalysts containing Ni salts, H.sub.3PO.sub.4 and Al.sub.2O.sub.3; and U.S. Pat. No. 3,547,972 discloses the reaction of HCN and butadiene in the gas phase over a mixed metal catalyst containing copper chromite and activated copper chromite, which does yield a mixture of pentenenitriles, with 77-82% selectivities to 3-pentenenitrile and. . .

SUMM [0005] Several patents teach that reaction of HCN with butadiene, ethylene, propylene or butenes, and additionally with air or oxygen in the gas phase, over various supported metal-containing catalysts give rise to cyanated olefinic products. However, in the olefinic products so produced the olefinic double bond is usually conjugated. . .

SUMM [0010] The present invention provides a catalyzed gas phase process for the hydrocyanation of diolefinic compounds which is rapid, selective, and efficient. While certain solvents or diluents can be used in this process, they can be eliminated altogether. Furthermore, the catalyst composition is utilized as a stationary solid phase, which

can reduce the cost of catalyst synthesis, recovery, and recycle, as well as the disposal cost of by-product waste. A corollary benefit is the reduction of. . .

SUMM . . . HCN in the gas phase within a temperature range of 135° C. to 200° C. in the presence of a catalyst composition that is a supported copper (I) or (II) fluorinated alkylsulfonate complex. Preferably the support used in such a catalyst composition is selected from the group consisting of silica, alumina, and carbon; more preferably the support is silica or carbon. Preferably the fluorinated alkylsulfonate in the copper complex in the catalyst composition is trifluoromethylsulfonate.

SUMM . . . HCN in the gas phase within a temperature range of 135° C. to 200° C. in the presence of a catalyst composition that is a copper (I) or (II) complex supported on a fluorosulfonated support. Also preferably the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a Nafion® perfluorinated polymer or fluorosulfonic acid.

SUMM . . . involves dissolving at least one of HCN and 1,3-butadiene in a solvent, inert to the starting materials and to the catalyst composition under the reaction conditions, prior to being introduced into the reaction, with the solution being vaporized prior to its. . .

SUMM [0015] A catalyst composition useful in the practice of the present invention includes a copper (I) or (II) fluorinated alkylsulfonate complex supported on. . . anions. A preferred support is silica, alumina, carbon and the like. Commonly used techniques for treatment of supports with metal catalysts can be found in B. C. Gates, Heterogeneous Catalysis, Vol. 2, pp. 1-29, Ed. B. L. Shapiro, Texas A & M University Press, College Station, Tex., 1984. Typically, in. . . (II) fluorinated alkylsulfonate complex is dispersed on a silica, alumina or carbon support at a concentration sufficient to produce a catalyst composition, including the support, containing 0.3% wt. to 1.0% wt. copper by weight of the total of the composition.

SUMM [0017] Catalyst compositions useful in the practice of the present invention also include copper (I) or (II) complexes supported on a fluorosulfonated. . . R--SO.sub.3.sup.- groups, where R is as defined above or is --C.sub.nF.sub.2n--. Preferably the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a Nafion® perfluorinated polymer or fluorosulfonic acid. Such a composite is. . .

SUMM [0018] In the process of the invention, the catalyst composition is loaded into a tubular reactor, and a gaseous diolefinic compound, e.g., butadiene, and HCN are passed continuously over the solid catalyst composition at a temperature sufficiently high to maintain the starting materials as well as the reaction products in the gas. . . to maintain all of the reactants and products in the gas phase but low enough to prevent deterioration of the catalyst composition. The particular preferred temperature depends to some extent on the catalyst composition being used, the diolefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical. . .

SUMM . . . a neat vapor or as a preheated solution in a solvent, such as acetonitrile or toluene. Under atmospheric pressure, using nitrogen or another inert gas as a carrier, a temperature of from about 160° C. to 175° C. is typically used. Nitrogen is preferred because of its low cost. Gaseous oxygen, water vapor, or any other gaseous substance which could react with the HCN, the copper portion of the catalyst composition, or the starting diolefinic compound should be avoided. The reaction products are liquid at room temperature and are conveniently. . .

- SUMM . . . in the production of adiponitrile. Other suitable diolefinic compounds include diolefinic compounds substituted with groups which do not deactivate the catalyst composition, for example, cis and trans-1,3-pentadienes.
- SUMM . . . of the present invention, a reactor, such as a tubular reactor, is charged in an inert atmosphere with the desired catalyst composition. The reactor feed and exit lines are preferably purged with an inert gas, such as nitrogen, argon or helium. The reactor is then heated to the desired temperature, either under a continuous flow of inert gas or sealed from. . . the solvent should be gaseous at the reaction temperature and pressure and inert towards the diolefinic compound, HCN, and the catalyst. Such solvents include hydrocarbons such as hexane, benzene, or toluene, or nitriles such as acetonitrile. When the reactants are fed. . .
- SUMM . . . condense all products to liquids. The flow rate of the diolefinic compound preferably is such that its mole ratio to catalyst, per hour of continuous feed, is about 2:1 to 10:1. The mole ratio of the diolefinic compound to HCN normally. . .
- SUMM Preparation of Catalyst Compositions
- SUMM [0027] Copper(I) trifluoromethanesulfonate on Sibunit carbon 7 Inside a nitrogen filled glove box, 0.38 g (1 meq) copper(I) (acetonitrile).sub.4--trifluoromethanesulfonate (prepared according to: Kubas, G. J. Inorg. Synth. 1990, 28, 68-70) was dissolved into 5 mL dry acetonitrile. 1.0 g of 12-20 mesh size Sibunit carbon 7 (Borskov Inst. of Catalysis, Novosibirsk, Russia), dried previously at 850° C. for 5 hrs in dry helium, was added to the solution and then the slurry was stirred for 15 mins. The solvent was evaporated under vacuum. . . re-wetted with minimal acetonitrile and re-evaporated to help insure complete incorporation of the copper material into the carbon. The recovered catalyst composition was stored under nitrogen until it was loaded into the hydrocyanation reactor for testing.
- SUMM [0029] The procedure to prepare Composition 1 was repeated except substituting 1 g of dry (850° C. in helium for 5 hrs) 20-40 mesh carbon CX0648-1 from EM Science (480 S. Democrat Rd, Gibbstown, N.J. 08027) for the Sibunit. . .
- SUMM [0030] The procedure of example 1 was repeated except substituting 1 g of dry (500° C. in dry air for 1 hr) 10-20 mesh large pore silica-gel granules #89346 from Alfa Aesar (30 Bond Street, Ward Hill, Mass. 01835-8099). . .
- SUMM . . . except substituting 0.25 g copper(I) (acetonitrile).sub.4 hexafluoroantimonate (prepared according to: Kubas, op. cit.) for the trifluoromethane sulfonate salt. The final catalyst was dried in flowing helium at 150° C. for 1 hr then stored under nitrogen.
- SUMM . . . except substituting 0.25 g copper(I) (acetonitrile).sub.4 hexafluorophosphate (prepared according to: Kubas, op. cit.) for the trifluoromethane sulfonate salt. The final catalyst composition was dried in flowing helium at 150° C. for 1 hr then stored under nitrogen.
- SUMM [0037] 1 g of dry (850° C. helium for 5 hrs) EM carbon as described above was slurried into a solution of 0.25 g copper(II) nitrate hydrate dissolved in methanol. The slurry was stirred then evaporated to dryness. The impregnated carbon was then calcined in flowing helium at 300° C. for 1 hr and then cooled to 200° C. The gas flow was switched to hydrogen and held at 200° C. for 1 hr. The material was flushed with nitrogen and cooled and then stored under nitrogen until testing.
- SUMM Copper(I) Exchanged Zeolite Y
- SUMM [0038] 2 g of zeolite NaY (LZY-52 from Aldrich) was dried at 500° C. in flowing air for 4 hrs. This material was slurried

into a solution of 1.0 g copper(I) (acetonitrile)<sub>4</sub> trifluoromethanesulfonate in 25 mL dry acetonitrile in a nitrogen filled glove box and stirred for 16 hrs. The solid was filtered off and washed with acetonitrile before drying in flowing nitrogen at 200°C. for 2 hrs. The copper(I) exchnaged zeolite catalyst was stored under nitrogen until testing.

DETD [0039] An empty 0.25-inch (0.64 cm) diameter, 15-inch (37.5 cm) long stainless steel tubular reactor was placed in a nitrogen-filled glove box. A plug of glass wool was placed in the bottom end of the reactor, followed by the amount and type of catalyst composition shown in Table 1. A thermocouple was inserted into the top of the reactor. Both ends of the reactor. . . fittings, and the reactor was removed from the glove box and connected to stainless steel reactor feed lines purged with nitrogen. Attached to the outlet side of the reactor was a valve which could be switched to either a waste receiver. . . mm integral diameter, supplied by J&W Scientific, Folsom, Calif. The stationary phase was cyanopropyl (50%) methylpolysiloxane. Feed streams consisted of nitrogen, gaseous butadiene and, typically, an acetonitrile solution containing HCN and also including cyclohexane as an internal GC standard. The combined. . .

DETD . . . Examples 1.about.6. Control E shows complete inactivity for Cu(0) dispersed on carbon, and Control F shows that Cu(AN).sub.4OTf ion-exchanged into zeolite Y is nearly inactive, compared to high activity when dispersed on Sibunit carbon (Table 1, Example 1). Table 2 shows. . .

DETD . . . 100 times the ratio of GC area % (3PN+4PN+2M3BN)/GC area % (all PNs).

TABLE 1

## Gas-Phase Hydrocyanation of Butadiene, Examples 1-6

Example	Elapsed (Support)	Catalyst Composition	Catalyst Comp., g	Feed rate, m mole/hr	N.sub.2, Temp.,	
		% HCN	% Select.	BD. . .		
DETD	[0042]	(Cu, m eq.)				

TABLE 2

## Gas-Phase Hydrocyanation of Butadiene, Controls A-F

Example	Elapsed (Support)	Catalyst Composition	Catalyst Comp., g	Feed rate, milli mole/hr	N.sub.2, Temp.,	
		% HCN	% Select.	BD HCN	cc/min	° . .
.	3.5	0				
"	(EM Carbon)	[0.71]			185	5.8
"					100	8.8
F	Cu(AN).sub.4OTf	1.05	4.0	2.5	"	165 1.1
	trace					
	(Zeolite Y)	[0.9]				2.2
	0					

CLM What is claimed is:

- . . . compounds, comprising reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase in the presence of a catalyst composition comprising either: (a) a supported copper (I) or (II) fluorinated alkylsulfonate complex; or (b) a copper (I) or (II).
- . . .

- . . . of claim 1 wherein the diolefinic compound is substituted with at least one other group which does not deactivate the catalyst composition.
  - . . . at least one of HCN and 1,3-butadiene is dissolved in a solvent, inert to the starting materials and to the catalyst composition under the reaction conditions, prior to being introduced into the reaction, but the solution is vaporized prior to its. . .
  - . . . process of claim 11 wherein the flow rate of the diolefinic compound is such that its mole ratio to the catalyst composition, per hour of continuous feed, is between about 5:1 and about 100:1.
15. The process of claim 1 wherein the catalyst composition comprises Composition (a), a supported copper (I) or (II) fluorinated alkylsulfonate complex.
17. The process of claim 1 wherein the catalyst composition comprises Composition (b), a copper (I) or (II) complex supported on a fluorosulfonated support.
18. The process of claim 17 wherein the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a perfluorinated polymer or fluorosulfonic acid.
- IT 592-51-8P, 4-Pentenitrile 1647-11-6P, 2-Cyano-1-butene  
4635-87-4F, 3-Pentenitrile  
(copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
Butadiene, reactions  
(copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)
- TI Copper-catalyzed vapor phase hydrocyanation of diolefinic compounds|
- PI US 2003045740 A1 20030306 <--|  
US 6753440 B2 20040622|
- AB A catalyzed vapor phase process for the hydrocyanation of acyclic diolefinic compounds to olefinic nitriles is described in which the olefinic double bond is not conjugated to the triple bond of the cyano group, wherein a catalyst composition comprising supported copper salts is used.
- SUMM [0002] This invention generally relates to a gas phase process for the hydrocyanation of diolefinic compounds to produce nonconjugated acyclic nitriles. In particular, the invention relates to a gas phase process for the hydrocyanation of diolefinic compounds to produce nonconjugated acyclic nitriles utilizing catalyst compositions comprising copper salts, dispersed on supports, including carbon, silica, alumina and a variety of metal oxides.
- SUMM [0003] Catalytic hydrocyanation systems, particularly pertaining to the hydrocyanation of olefins, are known in the art. For example, liquid phase systems useful for the hydrocyanation of butadiene to form pentenenitriles (PNs) are known in the art, e.g., U.S. Pat. No. 3,766,237. As used in that patent and as will be used herein, the term "pentenenitrile" is intended to mean a cyanobutene. Likewise, "butenenitrile" means cyanopropene. The pentenenitriles so formed are further subjected to hydrocyanation and, in some cases isomerization, to form adiponitrile (ADN), a commercially important material in the manufacture of nylon.
- SUMM [0004] The overwhelming majority of prior art processes for the hydrocyanation of butadiene are conducted in the liquid phase, with all



attendant waste disposal problems. For example, U.S. Pat. No. 4,240,976 utilized copper halide as a catalyst; U.S. Pat. No. 4,230,634 utilized copper inorganic salts in the presence of organic nitriles; and U.K. Patent No. 2,077,260 used copper bonded to a peroxo group. Previous approaches toward carrying out gas phase hydrocyanation of olefinic compounds have usually started with monoolefinic, not diolefinic, compounds and have given rise primarily to saturated products, which could not be further hydrocyanated. For example, U.S. Pat. No. 3,584,029 teaches that propionitrile is prepared by reaction of HCN with ethylene over catalysts containing Ni salts, H.sub.3PO.sub.4 and Al.sub.2O.sub.3; and U.S. Pat. No. 3,547,972 discloses the reaction of HCN and butadiene in the gas phase over a mixed metal catalyst containing copper chromite and activated copper chromite, which does yield a mixture of pentenenitriles, with 77-82% selectivities to 3-pentenenitrile and 4-pentenenitrile. However, the reaction of U.S. Pat. No. 3,547,972 also requires a co-feed of HCl.

SUMM [0005] Several patents teach that reaction of HCN with butadiene, ethylene, propylene or butenes, and additionally with air or oxygen in the gas phase, over various supported metal-containing catalysts give rise to cyanated olefinic products. However, in the olefinic products so produced the olefinic double bond is usually conjugated with the triple bond of the cyano group, and, therefore, substantially useless for the production of adiponitrile. For example, see:

SUMM [0010] The present invention provides a catalyzed gas phase process for the hydrocyanation of diolefinic compounds which is rapid, selective, and efficient. While certain solvents or diluents can be used in this process, they can be eliminated altogether. Furthermore, the catalyst composition is utilized as a stationary solid phase, which can reduce the cost of catalyst synthesis, recovery, and recycle, as well as the disposal cost of by-product waste. A corollary benefit is the reduction of the cost of capital equipment needed for the process.

SUMM [0011] One embodiment of the invention is a process for the gas-phase hydrocyanation of diolefinic compounds comprising reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase within a temperature range of 135° C. to 200° C. in the presence of a catalyst composition that is a supported copper (I) or (II) fluorinated alkylsulfonate complex. Preferably the support used in such a catalyst composition is selected from the group consisting of silica, alumina, and carbon; more preferably the support is silica or carbon. Preferably the fluorinated alkylsulfonate in the copper complex in the catalyst composition is trifluoromethylsulfonate.

SUMM [0012] Another embodiment of the invention is a process for the gas-phase hydrocyanation of diolefinic compounds comprising reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase within a temperature range of 135° C. to 200° C. in the presence of a catalyst composition that is a copper (I) or (II) complex supported on a fluorosulfonated support. Also preferably the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a Nafion® perfluorinated polymer or fluorosulfonic acid.

SUMM [0014] A further embodiment of the invention involves the introduction of HCN and 1,3-butadiene into the reaction without a solvent or diluent. Yet a further embodiment involves dissolving at least one of HCN and 1,3-butadiene in a solvent, inert to the starting materials and to the catalyst composition under the reaction conditions, prior to being

introduced into the reaction, with the solution being vaporized prior to its entry into the reaction.

- SUMM [0015] A catalyst composition useful in the practice of the present invention includes a copper (I) or (II) fluorinated alkylsulfonate complex supported on a carrier that is neutral and has a low surface area. A complex is one or more metal cations together with its associated anions. A preferred support is silica, alumina, carbon and the like. Commonly used techniques for treatment of supports with metal catalysts can be found in B. C. Gates, *Heterogeneous Catalysis*, Vol. 2, pp. 1-29, Ed. B. L. Shapiro, Texas A & M University Press, College Station, Tex., 1984. Typically, in accordance with this invention, the copper (I) or (II) fluorinated alkylsulfonate complex is dispersed on a silica, alumina or carbon support at a concentration sufficient to produce a catalyst composition, including the support, containing 0.3% wt. to 1.0% wt. copper by weight of the total of the composition.
- SUMM [0017] Catalyst compositions useful in the practice of the present invention also include copper (I) or (II) complexes supported on a fluorosulfonated support. A fluorosulfonated support contains R--SO.sub.3.sup.- groups, where R is as defined above or is --C.sub.nF.sub.2n--. Preferably the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a Nafion® perfluorinated polymer or fluorosulfonic acid. Such a composite is more particularly described in U.S. Pat. Nos. 5,824,622, 5,916,837 and 5,948,946.
- SUMM [0018] In the process of the invention, the catalyst composition is loaded into a tubular reactor, and a gaseous diolefinic compound, e.g., butadiene, and HCN are passed continuously over the solid catalyst composition at a temperature sufficiently high to maintain the starting materials as well as the reaction products in the gas phase. The preferred temperature range is from about 135° C. to about 200° C., most preferably from about 155° C. to about 175° C. The temperature must be high enough to maintain all of the reactants and products in the gas phase but low enough to prevent deterioration of the catalyst composition. The particular preferred temperature depends to some extent on the catalyst composition being used, the diolefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical and can conveniently be from about 1-10 atmospheres (about 101.3 to about 1013 kPa). No practical benefit is obtained when operating above the upper limit of this pressure range.
- SUMM [0019] HCN and/or diolefinic compound starting materials can be delivered as a neat vapor or as a preheated solution in a solvent, such as acetonitrile or toluene. Under atmospheric pressure, using nitrogen or another inert gas as a carrier, a temperature of from about 160° C. to 175° C. is typically used. Nitrogen is preferred because of its low cost. Gaseous oxygen, water vapor, or any other gaseous substance which could react with the HCN, the copper portion of the catalyst composition, or the starting diolefinic compound should be avoided. The reaction products are liquid at room temperature and are conveniently recovered by cooling. Branched 2-methyl-3-butenenitrile can be separated from linear 3-pentenitrile and 4-pentenitrile by distillation.
- SUMM [0020] The diolefinic compound reactants used in this invention include primarily conjugated diolefins containing from 4 to 10 carbon atoms; for

example 1,3-butadiene and cis and trans-2,4-hexadienes. Butadiene is especially preferred by reason of its commercial importance in the production of adiponitrile. Other suitable diolefinic compounds include diolefinic compounds substituted with groups which do not deactivate the catalyst composition, for example, cis and trans-1,3-pentadienes.

SUMM [0024] In the practice of the hydrocyanation process of the present invention, a reactor, such as a tubular reactor, is charged in an inert atmosphere with the desired catalyst composition. The reactor feed and exit lines are preferably purged with an inert gas, such as nitrogen, argon or helium. The reactor is then heated to the desired temperature, either under a continuous flow of inert gas or sealed from the ambient atmosphere. The reactor is fed with the desired diolefinic compound and HCN. These may be fed together or separately, either neat or as solutions in suitable solvents, such as acetonitrile or toluene. The hydrocyanation reaction is, however, preferably carried out without a solvent. If any solvent is used, the solvent should be gaseous at the reaction temperature and pressure and inert towards the diolefinic compound, HCN, and the catalyst. Such solvents include hydrocarbons such as hexane, benzene, or toluene, or nitriles such as acetonitrile. When the reactants are fed continuously, an inert gas carrier normally is employed as well.

SUMM [0025] The diolefinic compound, HCN and any solvent are passed through a heated portion of feed line heated to the reaction temperature to ensure complete vaporization. The gaseous product mixture exiting the reactor can be passed, if desired, through a heated gas sampling loop of a gas chromatograph for periodically monitoring the progress of the reaction. Alternatively, the gaseous effluent can be cooled to about 0° C. to 25° C. in order to condense all products to liquids. The flow rate of the diolefinic compound preferably is such that its mole ratio to catalyst, per hour of continuous feed, is about 2:1 to 10:1. The mole ratio of the diolefinic compound to HCN normally is at least about 1:1.

SUMM Preparation of Catalyst Compositions

SUMM [0027] Copper(I) trifluoromethanesulfonate on Sibunit carbon 7 Inside a nitrogen filled glove box, 0.38 g (1 meq) copper(I) (acetonitrile).sub.4--trifluoromethanesulfonate (prepared according to: Kubas, G. J. Inorg. Synth. 1990, 28, 68-70) was dissolved into 5 mL dry acetonitrile. 1.0 g of 12-20 mesh size Sibunit carbon 7 (Borekov Inst. of Catalysis, Novosibirsk, Russia), dried previously at 850° C. for 5 hrs in dry helium, was added to the solution and then the slurry was stirred for 15 mins. The solvent was evaporated under vacuum and the resulting solid was re-wetted with minimal acetonitrile and re-evaporated to help insure complete incorporation of the copper material into the carbon. The recovered catalyst composition was stored under nitrogen until it was loaded into the hydrocyanation reactor for testing.

SUMM [0029] The procedure to prepare Composition 1 was repeated except substituting 1 g of dry (850° C. in helium for 5 hrs) 20-40 mesh carbon CX0648-1 from EM Science (480 S. Democrat Rd, Gibbstown, N.J. 08027) for the Sibunit 7 carbon.

SUMM [0030] The procedure of example 1 was repeated except substituting 1 g of dry (500° C. in dry air for 1 hr) 10-20 mesh large pore silica-gel granules #89346 from Alfa Aesar (30 Bond Street, Ward Hill,

Mass. 01835-8099) for the Sibunit 7 carbon.

- SUMM [0034] The procedure to prepare Composition 3 was repeated except substituting 0.25 g copper(I) (acetonitrile).sub.4 hexafluoroantimonate (prepared according to: Kubas, op. cit.) for the trifluoromethane sulfonate salt. The final catalyst was dried in flowing helium at 150° C. for 1 hr then stored under nitrogen.
- SUMM [0035] The procedure to prepare Composition 3 was repeated except substituting 0.25 g copper(I) (acetonitrile).sub.4 hexafluorophosphate (prepared according to: Kubas, op. cit.) for the trifluoromethane sulfonate salt. The final catalyst composition was dried in flowing helium at 150° C. for 1 hr then stored under nitrogen.
- SUMM [0037] 1 g of dry (850° C. helium for 5 hrs) EM carbon as described above was slurried into a solution of 0.25 g copper(II) nitrate hydrate dissolved in methanol. The slurry was stirred then evaporated to dryness. The impregnated carbon was then calcined in flowing helium at 300° C. for 1 hr and then cooled to 200° C. The gas flow was switched to hydrogen and held at 200° C. for 1 hr. The material was flushed with nitrogen and cooled and then stored under nitrogen until testing.
- SUMM Copper(I) Exchanged Zeolite Y
- SUMM [0038] 2 g of zeolite NaY (LZY-52 from Aldrich) was dried at 500° C. in flowing air for 4 hrs. This material was slurried into a solution of 1.0 g copper(I) (acetonitrile)<sub>4</sub> trifluoromethanesulfonate in 25 mL dry acetonitrile in a nitrogen filled glove box and stirred for 16 hrs. The solid was filtered off and washed with acetonitrile before drying in flowing nitrogen at 200° C. for 2 hrs. The copper(I) exchanged zeolite catalyst was stored under nitrogen until testing.
- DETD [0039] An empty 0.25-inch (0.64 cm) diameter, 15-inch (37.5 cm) long stainless steel tubular reactor was placed in a nitrogen-filled glove box. A plug of glass wool was placed in the bottom end of the reactor, followed by the amount and type of catalyst composition shown in Table 1. A thermocouple was inserted into the top of the reactor. Both ends of the reactor were sealed with metal fittings, and the reactor was removed from the glove box and connected to stainless steel reactor feed lines purged with nitrogen. Attached to the outlet side of the reactor was a valve which could be switched to either a waste receiver or a heated tubing line for diverting the gaseous effluent to an injector for analysis by gas chromatography (GC). GC analyses were done on a 30 m DB-23 capillary column of a 0.32 mm integral diameter, supplied by J&W Scientific, Folsom, Calif. The stationary phase was cyanopropyl (50%) methylpolysiloxane. Feed streams consisted of nitrogen, gaseous butadiene and, typically, an acetonitrile solution containing HCN and also including cyclohexane as an internal GC standard. The combined feed streams were preheated to 150° C. to ensure complete vaporization. The reactor was heated in a split tube furnace to the temperatures shown in Table 1. Product samples were collected, generally every hour. Table 1 shows the specific reaction conditions and summarizes the results.
- DETD [0040] Controls A.about.F show comparative versions of the hydrocyanation of butadiene using several Cu(I) salts dispersed on carbon which are either inactive or exhibit short-lived low activity. Controls A.about.F were run under a process comparable to that of

Examples 1.about.6. Control E shows complete inactivity for Cu(0) dispersed on carbon, and Control F shows that Cu(AN).sub.4OTf ion-exchanged into zeolite Y is nearly inactive, compared to high activity when dispersed on Sibunit carbon (Table 1, Example 1). Table 2 shows the specific reaction conditions and summarizes the results.

DETD [0041] Percent conversion of HCN was calculated as (measured GC area % for PNs/measured GC area % for cyclohexane) $\times$ (GC response factor for PNs) $\times$ (mmoles of cyclohexane fed per hour/mmoles of HCN fed per hour) $\times$ 100. Response factor is the number, characteristic for each compound, required for converting area percent to mole percent of PNs. Percent Linear was determined as 100 times the ratio of GC area % (3PN+4PN)/GC area % (3PN+4PN+2M3BN). Percent selectivity to useful PNs (3PN+4PN+2M3BN) was determined as 100 times the ratio of GC area % (3PN+4PN+2M3BN)/GC area % (all PNs).

TABLE 1

Gas-Phase Hydrocyanation of Butadiene, Examples 1-6								
Example	Catalyst Composition		Catalyst Comp., g		Feed rate, m mole/hr		N.sub.2, Temp.,	
	Elapsed time, hr	(Support) % Linear	% HCN Conv.	% Select. (Cu, m eq.) Useful PNs	BD	HCN	cc/min	° C.
1	Cu(AN).sub.4OTf		1.03		2.1	1.1	5	175
	88.9	56.2	100					
	(Sibunit Carbon)	(1.0)						
	88.2	81.6	"					3.2
5.2	91.1	99.5	"					
7.2	92.8	78.4	"					
9.3	91.9	64.5	"					
11.3	89.2	54.1	"					
13.3	90.0	51.4	"					
15.4	91.7	39.5	"					
2	Cu(OTf).sub.2		1.6		2.1	1.1	5	175
	84.2	48.5	100					
	(Sibunit		(1.0)					
	84.0	40.9	"					3
	Carbon)							
	86.7	49.8	"					5
7	91.2	69.7	"					
9.1	90.8	89.6	"					
11.1	90.5	81.7	"					
13.1	90.9	66.5	"					
15.1	89.0	58.5	"					
3	Cu(AN).sub.4OTf		1.48		4.0	2.9	0	160
	88.2	24.5	100					
	(EM Carbon)	(1.0)						
	90.3	33.3	"					2.8
3.8	90.0	20.1	"					
4.8	90.0	11.6	"					
22.3		0.9	"					
4	Cu(AN).sub.4OTf		1.33		2.1	1.2	5	175
	88.5	41.4	100					
	(Silica)	(1.0)						
	88.8	83.9	"					2.5
6.5	89.0	65.8	"					
12.5	87.9	50.0	"					
17.5	88.8	38.1	"					

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21.5	93.2	33.4	"					
5	Cu(AN).sub.4OTf		1.19	2.1	1.2	5	175	1
	87.8	78.9	100					
	(Nafion ®/Silica) (1.0)							
	2.5	90.2	97.1	"				
5.1	90.1	88.8	"					
9.1	87.1	96.5	"					
16.1	90.2	72.6	"					
20.1	89.2	52.7	"					
24.5	89.3	34.1	"					
6	Cu(AN).sub.4OTf		1.63	2.1	1.2	5	175	0.5
	45.5	14	100					
	(derivatized [ ]							3.5
	86.2	105.4	"					
	Silica)							6.5
	91.5	98.7	"					
12.5	90.6	88.9	"					
19.5	90.3	78.4	"					
24.5	88.4	56.3	"					
DETD	[0042]							
TABLE 2								

## Gas-Phase Hydrocyanation of Butadiene, Controls A-F

Example	Catalyst Composition			Catalyst Comp., g		Feed rate, milli mole/hr		N.sub.2, Temp.,	
	Elapsed (Support) time, hr	% Linear	% HCN (Cu, m eq.) Conv.	% Select. BD HCN Useful PNs	cc/min	° C.			
A	Cu(tosylate)	1.36	4.0	2.9	0	160	1		
	2.0	100							
	(EM Carbon)	(1.0)						2	
	3.3	"							
4		1.4	"						
5		1.0	"						
B	Cu(AN).sub.4SbF.sub.6	0.62	5.4	2.6	"	165	1		
	trace								
	(EM Carbon)	[0.27]	"	1.3	"	"	3		
	"		"	"	"	185	5.6		
	0								
C	Cu(AN).sub.4PF.sub.6	0.5	5.4	1.0	"	165	1		
	0								
	(EM Carbon)	[0.27]					3		
	"								
5		"							
D	CuCl	1.14	4.0	2.9	"	160	2.2		
	1.8								
	(EM Carbon)	(1.0)				"	3.3		
	1.3								
						180	5.1		
	0.6					"	6.2		
	0.3								
E	Cu(O)	0.58	5.4	2.6	"	165	3.5		
	0								
	(EM Carbon)	[0.71]				185	5.8		
	"								

	"					100	8.8
F	Cu(AN).sub.4OTf	1.05	4.0	2.5	"	165	1.1
	trace						
	(Zeolite Y)	[0.9]					2.2

0

1. A process for the gas-phase hydrocyanation of diolefinic compounds, comprising reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase in the presence of a catalyst composition comprising either: (a) a supported copper (I) or (II) fluorinated alkylsulfonate complex; or (b) a copper (I) or (II) complex supported on a fluorosulfonated support.

7. The process of claim 1 wherein the diolefinic compound is substituted with at least one other group which does not deactivate the catalyst composition.

9. The process of claim 7 wherein at least one of HCN and 1,3-butadiene is dissolved in a solvent, inert to the starting materials and to the catalyst composition under the reaction conditions, prior to being introduced into the reaction, but the solution is vaporized prior to its entry into the reaction.

12. The process of claim 11 wherein the flow rate of the diolefinic compound is such that its mole ratio to the catalyst composition, per hour of continuous feed, is between about 5:1 and about 100:1.

15. The process of claim 1 wherein the catalyst composition comprises Composition (a), a supported copper (I) or (II) fluorinated alkylsulfonate complex.

17. The process of claim 1 wherein the catalyst composition comprises Composition (b), a copper (I) or (II) complex supported on a fluorosulfonated support.

18. The process of claim 17 wherein the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a perfluorinated polymer or fluorosulfonic acid.

IT	592-51-8P, 4-Pentenitrile	1647-11-6P, 2-Cyano-1-butene
	4635-87-4P, 3-Pentenitrile	
	(copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)	
IT	74-90-8, Hydrogen cyanide, reactions 106-99-0,	
	Butadiene, reactions	
	(copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)	
IT	4635-87-4P, 3-Pentenitrile	
	(copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)	
RN	4635-87-4	USPATFULL
CN	3-Pentenitrile	(CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,

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Butadiene, reactions

(copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 54 OF 60 USPATFULL on STN

ACCESSION NUMBER: 2003:47857 USPATFULL Full-text

TITLE: Catalyst comprising a complex of a metal from subgroup VIII based on a bidentate phosphonite ligand, and method for producing nitriles

INVENTOR(S): Fischer, Jakob, Kirchdorf, GERMANY, FEDERAL REPUBLIC OF  
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PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Ludwigshafen, GERMANY, FEDERAL REPUBLIC OF (non-U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 6521778	B1	20030218	<--
	WO 9964155		19991216	
APPLICATION INFO.:	US 2000-701601		20001130	(9)
	WO 1999-EP3888		19990604	

	NUMBER	DATE
PRIORITY INFORMATION:	DE 1998-19825212	19980605
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	GRANTED	
PRIMARY EXAMINER:	McKane, Joseph K.	
ASSISTANT EXAMINER:	Anderson, Rebecca	
LEGAL REPRESENTATIVE:	Keil & Weinkauff	
NUMBER OF CLAIMS:	14	
EXEMPLARY CLAIM:	1	
NUMBER OF DRAWINGS:	0 Drawing Figure(s); 0 Drawing Page(s)	
LINE COUNT:	934	

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A catalyst which comprises at least one complex of a metal of subgroup VIII having at least one bidentate phosphonite ligand of the formula I ##STR1##



or salts and mixtures thereof, a process for the preparation of mixtures of monoolefinic C.sub.5-monoitriles, a process for the catalytic isomerization of branched aliphatic monoalkenenitriles and a process for the preparation of adiponitrile.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

- TI Catalyst comprising a complex of a metal from subgroup VIII based on a bidentate phosphonite ligand, and method for producing nitriles
- AB A catalyst which comprises at least one complex of a metal of subgroup VIII having at least one bidentate phosphonite ligand of. . .
- AB or salts and mixtures thereof, a process for the preparation of mixtures of monoolefinic C.sub.5-monoitriles, a process for the catalytic isomerization of branched aliphatic monoalkenenitriles and a process for the preparation of adiponitrile.
- SUMM The present invention relates to a catalyst which comprises a complex of a metal of subgroup VIII, which comprises at least one bidentate phosphonite ligand, a process for the preparation of mixtures of monoolefinic C.sub.5-monoitriles and a process for the preparation of adipodinitrile by catalytic hydrocyanation in the presence of such a catalyst.
- SUMM "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1, VCH Weinheim, page 465 et seq., describes in general the addition reaction of hydrogen cyanide with olefins under heterogeneous and homogeneous catalysis. In particular, catalysts based on phosphine, phosphite and phosphinite complexes of nickel and of palladium are used. For the preparation of adipodinitrile by hydrocyanation of butadiene, predominantly nickel(0) phosphite catalysts are used, in the presence or absence of a Lewis acid as a promoter.
- SUMM J. Chem. Soc., Chem. Commun., 1991, page 1292, describes chiral aryl diphosphites as ligands for hydrocyanation catalysts. In these ligands, the phosphite group is bonded via two of its oxygen atoms to the 3- and 3'-positions of. . .
- SUMM U.S. Pat. No. 5,449,807 describes a process for the gas-phase hydrocyanation of diolefins in the presence of a supported nickel catalyst based on at least one bidentate phosphite ligand, the two phosphite groups being bridged by an unsubstituted or substituted 2,2'-biphenyl. . . describes a process for the gas-phase isomerization of 2-alkyl-3-monoalkenenitriles to give linear 3- and/or 4-monoalkenenitriles in the presence of the catalysts described in U.S. Pat. No. 5,449,807.
- SUMM WO 95/14659 describes a process for the hydrocyanation of monoolefins, in which catalysts based on zero-valent nickel and bidentate phosphite ligands may be used. In these ligands, the phosphite groups together with two. . .
- SUMM U.S. Pat. No. 5,512,695 likewise describes a process for the hydrocyanation of monoolefins in the presence of a nickel catalyst which comprises a bidentate phosphite ligand.
- SUMM WO 96/11182 describes a process for hydrocyanation in the presence of a nickel catalyst based on a bidentate or polydentate phosphite ligand in which the phosphite groups are not part of a heterocycle. The. . .
- SUMM U.S. Pat. No. 5,523,453 describes a process for hydrocyanation in the presence of a nickel catalyst based on a bidentate ligand which comprises at least one phosphinite group and a further phosphorus-containing group which is selected. . . WO 97/23446 describes a process for the hydrocyanation of diolefins and for the isomerization of 2-alkyl-3-monoalkenenitriles in the presence of catalysts which correspond to those described in U.S. Pat. No.

- 5,523,453.
- SUMM . . . describes a process for the hydrocyanation of diolefinic compounds and for the isomerization of the resulting, nonconjugated 2-alkyl-3-monoalkenenitriles, a nickel(0) catalyst based on a polydentate phosphite ligand being used in the presence of a Lewis acid as promoter. The phosphite groups. . .
- SUMM None of the abovementioned publications describes hydrocyanation catalysts based on phosphonite ligands. In particular, no catalysts based on bidentate chelate phosphonites are described.
- SUMM . . . hydrocyanation of ethylenically unsaturated compounds which may have further functional groups, such as nitriles, in the presence of a nickel catalyst. These nickel catalysts carry four ligands of the formula M(X,Y,Z), where X, Y and Z, independently of one another, are each a radical. . . the hydrocyanation. On the other hand, it is not disclosed that phosphonites can be used as ligands for nickel(0) hydrocyanation catalysts. In particular, no bidentate chelate phosphonite ligands are described.
- SUMM It is an object of the present invention to provide novel catalysts based on a metal of subgroup VIII. They should preferably have good selectivity and good catalytic activity in the hydrocyanation of 1,3-butadiene and 1,3-butadiene-containing hydrocarbon mixtures. Preferably, they should also be suitable for the catalytic isomerization of monoalkenenitriles and for the addition reaction of the second molecule of hydrogen cyanide with said monoalkenenitriles, for example. . .
- SUMM We have surprisingly found that this object is achieved by catalysts based on a metal of subgroup VIII which comprise at least one bidentate phosphonite ligand.
- SUMM The present invention therefore relates to a catalyst comprising a complex of a metal of subgroup VIII, having a bidentate phosphonite ligand of the formula I ##STR2##
- SUMM The novel catalysts may have one or more of the phosphonite ligands of the formula I. In addition to the ligands of formula. . .
- SUMM Preferably, the metal of subgroup VIII is cobalt, rhodium, ruthenium, palladium or nickel. If the novel catalysts are used for hydrocyanation, the metal of subgroup VIII is in particular nickel.
- SUMM For the preparation of the phosphonite ligands of the formula I which are used in the novel catalysts, a dihalophosphorus(III) compound III, where R.sub.1 (or R.sub.1') has the abovementioned meanings, can first be reacted with a monoalcohol IV,. . .
- SUMM For the preparation of the novel catalysts, at least one phosphonite ligand of the formula I can be reacted with a metal of subgroup VIII, e.g. nickel,. . .
- SUMM . . . haloalkanes, for example dichloromethane, chloroform, dichloroethane and trichloroethane. Other suitable solvents are the liquid starting materials and/or products of the catalyzed reaction. The temperature is from -70 to 150° C., preferably from 0° C. to 100° C., particularly preferably about room. . .
- SUMM . . . the form of a powder. The reaction of nickel and phosphonite ligand is preferably effected in a product of the catalyzed reaction, such as the hydrocyanation reaction, as the solvent, for example in a mixture of monoolefinic C.sub.5-monoalkenenitriles or, preferably, in. . .
- SUMM . . . relates to a process for the preparation of mixtures of monoolefinic C.sub.5-monoalkenenitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, wherein the hydrocyanation is carried out in the presence of at least one of the novel catalysts described above.
- SUMM . . . be obtained in which a C.dbd.C double bond is present in conjugation with the C.tbd.N bond. These may act as catalyst poisons

for the first reaction step of the adipic acid preparation, the monoaddition reaction of hydrogen cyanide.

SUMM If required, those components which may give rise to catalyst poisons, in particular alkynes, 1,2-dienes and mixtures thereof, are therefore partially or completely removed from the hydrocarbon mixture. To remove these components, the C.sub.4 cut is subjected to a partial catalytic hydrogenation before the addition reaction with hydrogen cyanide. This partial hydrogenation is effected in the presence of a hydrogenation catalyst which is capable of hydrogenating alkynes and 1,2-dienes selectively alongside other dienes and monoolefins.

SUMM Suitable heterogeneous catalyst systems for the selective hydrogenation are known and comprise in general a transition metal compound on an inert support. They. . . particular those described in U.S. Pat. Nos. 4,587,369, 4,704,492 and 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on copper are sold by Dow Chemical as KLP catalyst.

SUMM . . . der technischen Chemie, Vol. 1, 3rd edition, 1951, page 743 et seq. and page 769 et seq. Preferably, a stirred catalyst cascade or a tube reactor is used for a continuous process.

SUMM . . . reactor with 1,3-butadiene or with the hydrocarbon mixture, if required, a part of the hydrogen cyanide and a novel hydrocyanation catalyst which may have been produced in situ and, if required, a solvent. Suitable solvents are those mentioned above for the preparation of the novel catalysts, preferably aromatic hydrocarbons, such as toluene or xylene, or tetrahydrofuran.

SUMM . . . extraction, and working-up of the remaining reaction mixture by distillation to isolate the desired products and recover the still active catalyst.

SUMM . . . and hydrocyanic acid are fed to a reactor via separate feeds at the rate at which they are consumed. The catalysts can be fed in together with one of the starting materials or via a separate feed. Suitable, preferably thoroughly mixable reactors are likewise known to a person skilled in the art. They include, for example, stirred catalysts, catalytic cascades and tube reactors, which, if required, are provided with an internal lining. The working-up of the reaction products, too, . . .

SUMM . . . an isomerization additionally takes place at higher reaction temperatures and/or during longer reaction times in the presence of the novel catalysts, the 3-pentenitrile/2-methyl-3-butenitrile ratio obtained then generally being about 2:1, preferably about 5:1, in particular about 8:1.

SUMM . . . fraction of 3-pentenitrile or 4-pentenitrile and a very small fraction of conjugated 2-pentenitrile and 2-methyl-2-butenitrile which may act as a catalyst poison should be formed.

SUMM The novel catalysts based on phosphonite ligands are also advantageous for the positional and double bond isomerization in step 2 and/or the addition. . .

SUMM The present invention therefore furthermore relates to a process for the catalytic isomerization of branched aliphatic monoalkenenitriles having a nonconjugated C.dbd.C and C.tbd.N bond to give linear monoalkenenitriles, wherein the isomerization is carried out in the presence of a novel catalyst.

SUMM . . . aliphatic, nonconjugated 2-alkyl-3-monoalkenenitriles and in particular 2-methyl-3-butenitrile. Mixtures of monoolefinic C.sub.5-monoenitriles, as obtainable by the process, described above, for the catalytic hydrocyanation of butadiene or of 1,3-butadiene-containing hydrocarbon mixtures, are preferably used for the isomerization. Advantageously, the novel catalysts exhibit good activity with respect to the formation of linear monoalkene nitriles. The isomerization can, if desired, be effected in the presence of a

conventional promoter, for example a Lewis acid, such as  $\text{AlCl}_3$  or  $\text{ZnCl}_2$ . Advantageously, the novel catalysts generally permit isomerization without the addition of a promoter. The selectivity of the novel catalysts in the isomerization without the addition of a promoter is in general higher than that with the addition of a promoter. Furthermore, expensive removal of the promoter of the isomerization can be dispensed with. Thus, in principle only one catalyst circulation for hydrocyanation, isomerization and, if required, an addition reaction of a second molecule of hydrogen cyanide is required. Dispensing. . .

SUMM The present invention furthermore relates to a process for the preparation of adipodinitrile by catalytic hydrocyanation of linear monoolefinic C.sub.5-mononitriles, wherein the hydrocyanation is carried out in the presence of a novel catalyst. Advantageously, a mixture of monoolefinic C.sub.5-mononitriles which is obtainable by the novel process for the catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture and which, if required, was additionally subjected to working up and/or. . .

SUMM In a suitable embodiment of the novel process for the preparation of adipodinitrile, the catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture (Step 1) and the isomerization (Step 2) are carried out in. . . separate reactors, where, for example, after the end of the monoaddition reaction of hydrogen cyanide in a first reactor, the catalyst-containing reaction mixture is transferred, without isolation and working up, to a second reactor and is isomerized therein.

SUMM a) preparation of a mixture of monoolefinic C.sub.5-mononitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture,

SUMM b) catalytic isomerization of the mixture from a), and

SUMM c) catalytic hydrocyanation of the isomerized mixture from b), wherein the steps a), b) and c) are carried out in the presence of at least one novel catalyst and without isolation of the product or products from step a) and/or b).

SUMM The novel catalysts can be prepared simply and thus economically from readily obtainable intermediates, some of which are commercially available. Advantageously, they have. . . in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures. In general, they have higher stability relative to hydrogen cyanide than conventional hydrocyanation catalysts and, in the hydrocyanation, an excess of hydrogen cyanide can also be added to said catalysts without resulting in marked deposition of inactive nickel(II) compounds, e.g. nickel(II) cyanide. In contrast to known hydrocyanation catalysts based on non-complex phosphine and phosphite ligands, the novel catalysts are therefore suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide in the reaction mixture. . . also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. Thus, the catalysts used according to the invention and the hydrocyanation processes based on them generally have higher catalyst recycling rates and longer catalyst on-stream times than known processes. This is advantageous not only for achieving better cost-efficiency but also from ecological points of view, since the nickel cyanide formed from the active catalyst with hydrogen cyanide is highly toxic and must be worked up or disposed of at high cost. Moreover, in the preparation of the novel catalysts, generally no excess or a smaller excess of ligand is required relative to the metal of subgroup VIII than in the case of conventional catalysts.

SUMM In addition to the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures, the catalysts of the formula I are generally suitable for all conventional hydrocyanation processes. In particular,

- the hydrocyanation of nonactivated olefins, for. . .
- SUMM The catalysts which are described above and comprise chiral phosphonite ligands of the formula I are suitable for enantioselective hydrocyanation.
- DETD 0.41 g (1.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0), 2.14 g of ligand I and 10 ml of toluene are initially taken under argon at room temperature in a glass autoclave and stirred for 10 minutes, the reaction batch acquiring a red-brown color. A. . .
- DETD . . . g (1.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0), 2.9 g of ligand II and 10 g of toluene are initially taken under an argon atmosphere at room temperature in a glass autoclave and stirred for 10 minutes, the reaction batch acquiring a red-brown color. . .
- DETD . . . g of ligand I, 15 ml of toluene and 0.14 g (0.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0) are initially taken under an argon atmosphere and stirred at room temperature for 45 minutes. The catalyst complex which forms is precipitated from the initially homogeneous solution. The volatile components are removed at highly superatmospheric pressure. 40.5. . .
- DETD As demonstrated by Example 3, isomerization using the novel catalysts is also possible without the addition of a promoter.
- DETD . . . g of ligand II, 8 ml of toluene and 0.07 g (0.25 mmol) of bis(1,5-cyclooctadienyl)nickel(0) are initially taken under an argon atmosphere and stirred at room temperature for 30 minutes. Some of the catalyst complex which forms is precipitated from the initially red homogeneous solution. The volatile components are removed at highly superatmospheric pressure. . .
- CLM What is claimed is:
1. A catalyst composition comprising a complex of a metal of group VIII, and a bidentate phosphonite ligand of the formula I ##STR10##. .
  2. The catalyst composition as claimed in claim 1, A being a radical of the formulae II.1 to II-5 ##STR11## where X is. . .
  3. The catalyst composition as claimed in claim 1, R.sup.1 and R.sup.1', independently of one another, being alkyl or aryl.
  4. The catalyst composition as claimed in claim 1, R.sup.2 and R.sup.2', independently of one another, each being phenyl substituents which may have. . .
  5. The catalyst composition as claimed in claim 1, the phosphonite ligand of the formula I being selected from ligands of the formulae. .
  6. The catalyst composition as claimed in claim 1, which additionally has at least one further ligand selected from cyanide, halides, amines, carboxylates,. . .
  7. The catalyst composition as claimed in claim 1, the metal of group VIII being cobalt, rhodium, ruthenium, palladium or nickel.
  8. . .
  9. A process for the preparation of a mixture of monoolefinic C.sub.5-mono nitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, wherein the hydrocyanation is carried out in the presence of a catalyst composition as claimed in claim 1.
  10. A process for the catalytic isomerization of branched aliphatic monoalkenenitriles having a nonconjugated C.dbd.C and C.tbd.N bond to give linear monoalkenenitriles, wherein the isomerization is carried out in the presence of a catalyst composition as claimed in claim 1.
  11. A process for the preparation of adipodinitrile by catalytic hydrocyanation of a linear monoolefinic C.sub.5-mono nitrile, wherein the

hydrocyanation is carried out in the presence of a catalyst composition as claimed in claim 1.

. . . preparation of adipodinitrile, comprising a) preparation of a mixture of monoolefinic C.sub.5-mono nitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene- containing hydrocarbon mixture, b) catalytic isomerization of the mixture from a), and c) catalytic hydrocyanation of the isomerized mixture from b), wherein the steps a), b) and c) are carried out in the presence of at least one catalyst composition as claimed in claim 1 and without isolation of the product or products from step a) and/or b).

. . . of olefins, wherein the hydrocyanation and/or positional and double-bond isomerization of olefins is carried out in the presence of a catalyst composition as claimed in claim 1.

14. The catalyst composition as claimed in claim 3, wherein R.sup.1 and R.sup.1', independently of one another, are selected from the group consisting of . . .

IT 74-90-8, Hydrocyanic acid, reactions

(hydrocyanation of butadiene; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 106-99-0, 1,3-Butadiene, reactions

(hydrocyanation; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 4635-87-4F, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile

(manufacture and isomerization; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

TI Catalyst comprising a complex of a metal from subgroup VIII based on a bidentate phosphonite ligand, and method for producing nitriles|

PI US 6521778

B1 20030218

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WO 9964155 19991216|

AB A catalyst which comprises at least one complex of a metal of subgroup VIII having at least one bidentate phosphonite ligand of the formula I ##STR1##|

AB or salts and mixtures thereof, a process for the preparation of mixtures of monoolefinic C.sub.5-mono nitriles, a process for the catalytic isomerization of branched aliphatic monoalkenenitriles and a process for the preparation of adiponitrile.|

SUMM The present invention relates to a catalyst which comprises a complex of a metal of subgroup VIII, which comprises at least one bidentate phosphonite ligand, a process for the preparation of mixtures of monoolefinic C.sub.5-mono nitriles and a process for the preparation of adipodinitrile by catalytic hydrocyanation in the presence of such a catalyst.

SUMM "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1, VCH Weinheim, page 465 et seq., describes in general the addition reaction of hydrogen cyanide with olefins under heterogeneous and homogeneous catalysis. In particular, catalysts based on phosphine, phosphite and phosphinite complexes of nickel and of palladium are used. For the preparation of adipodinitrile by hydrocyanation of butadiene, predominantly nickel(0) phosphite catalysts are used, in the presence or absence of a Lewis acid as a promoter.

SUMM J. Chem. Soc., Chem. Commun., 1991, page 1292, describes chiral aryl diphosphites as ligands for hydrocyanation catalysts. In these ligands, the phosphite group is bonded via two of its oxygen atoms to the 3- and 3'-positions of a 2,2'-binaphthyl unit, with which it thus

forms a 7-membered heterocycle. In addition, two of these heterocycles may likewise be linked via a 2,2'-binaphthyl unit to form a bidentate chelate ligand. In J. Chem. Soc., Chem. Commun., 1991, page 803 et seq., analogous chelate diphosphite complexes of nickel(0) and platinum(0) are described for this purpose, a 2,2'-biphenyl unit being used instead of a 2,2'-binaphthyl unit as the bridging group.

- SUMM U.S. Pat. No. 5,449,807 describes a process for the gas-phase hydrocyanation of diolefins in the presence of a supported nickel catalyst based on at least one bidentate phosphite ligand, the two phosphite groups being bridged by an unsubstituted or substituted 2,2'-biphenyl group. U.S. Pat. No. 5,440,067 describes a process for the gas-phase isomerization of 2-alkyl-3-monoalkenenitriles to give linear 3- and/or 4-monoalkenenitriles in the presence of the catalysts described in U.S. Pat. No. 5,449,807.
- SUMM WO 95/14659 describes a process for the hydrocyanation of monoolefins, in which catalysts based on zero-valent nickel and bidentate phosphite ligands may be used. In these ligands, the phosphite groups together with two of their oxygen atoms are part of an aryl-fused 7-membered heterocycle. Pairs of these phosphite groups are then bridged by aryl-fused alkylene groups via the oxygen atoms which are not part of the heterocycle.
- SUMM U.S. Pat. No. 5,512,695 likewise describes a process for the hydrocyanation of monoolefins in the presence of a nickel catalyst which comprises a bidentate phosphite ligand.
- SUMM WO 96/11182 describes a process for hydrocyanation in the presence of a nickel catalyst based on a bidentate or polydentate phosphite ligand in which the phosphite groups are not part of a heterocycle. The groups used for bridging the phosphite groups correspond to those described in WO 95/14659.
- SUMM U.S. Pat. No. 5,523,453 describes a process for hydrocyanation in the presence of a nickel catalyst based on a bidentate ligand which comprises at least one phosphinite group and a further phosphorus-containing group which is selected from phosphinites and phosphites. The two phosphorus-containing groups of these bidentate ligands are in turn bridged via aryl-fused groups. WO 97/23446 describes a process for the hydrocyanation of diolefins and for the isomerization of 2-alkyl-3-monoalkenenitriles in the presence of catalysts which correspond to those described in U.S. Pat. No. 5,523,453.
- SUMM WO 96/22968 likewise describes a process for the hydrocyanation of diolefinic compounds and for the isomerization of the resulting, nonconjugated 2-alkyl-3-monoalkenenitriles, a nickel(0) catalyst based on a polydentate phosphite ligand being used in the presence of a Lewis acid as promoter. The phosphite groups of these polydentate ligands are once again components of aryl-fused heterocycles and may be bridged via aryl-fused groups.
- SUMM None of the abovementioned publications describes hydrocyanation catalysts based on phosphonite ligands. In particular, no catalysts based on bidentate chelate phosphonites are described.
- SUMM U.S. Pat. No. 3,766,237 describes a process for the hydrocyanation of ethylenically unsaturated compounds which may have further functional groups, such as nitriles, in the presence of a nickel catalyst. These nickel catalysts carry four ligands of the formula  $M(X,Y,Z)$ , where X,

Y and Z, independently of one another, are each a radical R or OR and R is selected from alkyl and aryl groups of up to 18 carbon atoms. However, only phosphines and phosphites are mentioned explicitly and are used in the examples for the hydrocyanation. On the other hand, it is not disclosed that phosphonites can be used as ligands for nickel(0) hydrocyanation catalysts. In particular, no bidentate chelate phosphonite ligands are described.

- SUMM It is an object of the present invention to provide novel catalysts based on a metal of subgroup VIII. They should preferably have good selectivity and good catalytic activity in the hydrocyanation of 1,3-butadiene and 1,3-butadiene-containing hydrocarbon mixtures. Preferably, they should also be suitable for the catalytic isomerization of monoalkenenitriles and for the addition reaction of the second molecule of hydrogen cyanide with said monoalkenenitriles, for example for the preparation of adipodinitrile.
- SUMM We have surprisingly found that this object is achieved by catalysts based on a metal of subgroup VIII which comprise at least one bidentate phosphonite ligand.
- SUMM The present invention therefore relates to a catalyst comprising a complex of a metal of subgroup VIII, having a bidentate phosphonite ligand of the formula I ##STR2##
- SUMM The novel catalysts may have one or more of the phosphonite ligands of the formula I. In addition to the ligands of formula I which are described above, they may also have at least one further ligand which is selected from cyanide, halides, amines, carboxylates, acetylacetone, arylsulfonates, alkanesulfonates, hydride, CO, olefins, dienes, cycloolefins, nitrites, N-containing heterocycles, aromatics and heteroaromatics, ethers, PF.sub.3 and mono-, bi- and polydentate phosphine, phosphinite, phosphonite and phosphite ligands. These further ligands may likewise be mono-, bi- or polydentate and may have coordinate bonds to the metal of subgroup VIII. Suitable further phosphorus-containing ligands are, for example, the phosphine, phosphinite and phosphite ligands described above as prior art.
- SUMM Preferably, the metal of subgroup VIII is cobalt, rhodium, ruthenium, palladium or nickel. If the novel catalysts are used for hydrocyanation, the metal of subgroup VIII is in particular nickel.
- SUMM For the preparation of the phosphonite ligands of the formula I which are used in the novel catalysts, a dihalophosphorus(III) compound III, where R.sup.1 (or R.sup.1') has the abovementioned meanings, can first be reacted with a monoalcohol IV, where R.sup.2 (or R.sup.2') has the abovementioned meanings, to give a compound of the formula V, according to the following scheme. If desired, this compound V can be isolated and/or purified by known methods, e.g. by distillation, before the further reaction. The compound V is then reacted with a diol of the formula VI to give the bidentate phosphonite ligands of the formula (I). Where, in the formula (I), R.sup.1 is identical to R.sub.1' and R.sup.2 is identical to R.sub.2', two equivalents of the formula V can be reacted with one equivalent of the formula VI in a one-stage reaction. Otherwise, first one equivalent of the formula V is reacted with one equivalent of the formula VI and, after formation of the monocondensate, a second compound of the formula (V) Cl-PR.sup.1'-OR.sup.2' is added and is further reacted to give the phosphonite of the formula (I).  
##STR8##



- SUMM For the preparation of the novel catalysts, at least one phosphonite ligand of the formula I can be reacted with a metal of subgroup VIII, e.g. nickel, or with a compound of the metal in the presence of a reducing agent or a complex of the metal, in each case in an inert solvent. Suitable nickel compounds of, for example, compounds in which the transition metal assumes an oxidation state higher than 0 and which are reduced in situ during the reaction with the phosphonite ligand of the formula I, in the presence or absence of a suitable reducing agent. These include, for example, the halides, preferably the chlorides, and the acetates of the abovementioned transition metals. NiCl<sub>2</sub>·sub.2 is preferably used. Suitable reducing agents are, for example, metals, preferably alkali metals, such as Na and K, aluminum, zinc and trialkylaluminum compounds.
- SUMM Suitable inert solvents for the preparation of the nickel(0) complexes are, for example, aromatics, such as benzene, toluene, ethylbenzene and chlorobenzene, ethers, preferably diethyl ether and tetrahydrofuran, and haloalkanes, for example dichloromethane, chloroform, dichloroethane and trichloroethane. Other suitable solvents are the liquid starting materials and/or products of the catalyzed reaction. The temperature is from -70 to 150° C., preferably from 0° C. to 100° C., particularly preferably about room temperature.
- SUMM If elemental nickel is used for the preparation of the phosphonite-nickel(0) complexes, it is preferably in the form of a powder. The reaction of nickel and phosphonite ligand is preferably effected in a product of the catalyzed reaction, such as the hydrocyanation reaction, as the solvent, for example in a mixture of monoolefinic C.sub.5-mono nitriles or, preferably, in 3-pentenitrile or 2-methyl-3-butenitrile. If required, the ligand may also be used as solvent. The temperature is from about 0 to 150° C., preferably 60 to 100° C.
- SUMM The present invention furthermore relates to a process for the preparation of mixtures of monoolefinic C.sub.5-mono nitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, wherein the hydrocyanation is carried out in the presence of at least one of the novel catalysts described above.
- SUMM C.sub.4 cuts are, if required, essentially freed from 1,2-dienes, such as propadiene, and from alkenynes, e.g. vinylacetylene, before the hydrocyanation of alkynes, such as propyne or butyne. Otherwise, products may be obtained in which a C.dbd.C double bond is present in conjugation with the C.tbd.N bond. These may act as catalyst poisons for the first reaction step of the adipic acid preparation, the monoaddition reaction of hydrogen cyanide.
- SUMM If required, those components which may give rise to catalyst poisons, in particular alkynes, 1,2-dienes and mixtures thereof, are therefore partially or completely removed from the hydrocarbon mixture. To remove these components, the C.sub.4 cut is subjected to a partial catalytic hydrogenation before the addition reaction with hydrogen cyanide. This partial hydrogenation is effected in the presence of a hydrogenation catalyst which is capable of hydrogenating alkynes and 1,2-dienes selectively alongside other dienes and monoolefins.
- SUMM Suitable heterogeneous catalyst systems for the selective hydrogenation are known and comprise in general a transition metal compound on an inert support. They are in particular those described in

U.S. Pat. Nos. 4,587,369, 4,704,492 and 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on copper are sold by Dow Chemical as KLP catalyst.

- SUMM Suitable reactors for the reaction are known to a person skilled in the art and are described, for example, in Ullmanns Enzyklopadie der technischen Chemie, Vol. 1, 3rd edition, 1951, page 743 et seq. and page 769 et seq. Preferably, a stirred catalyst cascade or a tube reactor is used for a continuous process.
- SUMM a) Filling a reactor with 1,3-butadiene or with the hydrocarbon mixture, if required, a part of the hydrogen cyanide and a novel hydrocyanation catalyst which may have been produced in situ and, if required, a solvent. Suitable solvents are those mentioned above for the preparation of the novel catalysts, preferably aromatic hydrocarbons, such as toluene or xylene, or tetrahydrofuran.
- SUMM c) If required, completion of the reaction by continued reaction and subsequent working up. To complete the reaction, the reaction time may be followed by a subsequent reaction time of from 0 minutes to about 5 hours, preferably from about 1 hour to 3.5 hours, in which hydrogen cyanide is no longer fed into the autoclaves. The temperature is left essentially constant at the previously set reaction temperature during this time. Working up is effected by conventional methods and comprises the removal of the unconverted 1,3-butadiene and of the unconverted hydrogen cyanide, for example by washing or extraction, and working-up of the remaining reaction mixture by distillation to isolate the desired products and recover the still active catalyst.
- SUMM The addition reaction of the hydrogen cyanide with 1,3-butadiene or a 1,3-butadiene-containing hydrocarbon mixture is preferably carried out continuously. The reaction is generally carried out so that essentially no relatively large amounts of unconverted hydrogen cyanide are present in the reactor. Suitable processes for the continuous hydrocyanation are known to a person skilled in the art. They include, for example, a feed process in which 1,3-butadiene and hydrocyanic acid are fed to a reactor via separate feeds at the rate at which they are consumed. The catalysts can be fed in together with one of the starting materials or via a separate feed. Suitable, preferably thoroughly mixable reactors are likewise known to a person skilled in the art. They include, for example, stirred catalysts, catalytic cascades and tube reactors, which, if required, are provided with an internal lining. The working-up of the reaction products, too, is preferably carried out by a conventional continuous method.
- SUMM In general, the 3-pentenitrile/2-methyl-3-butenitrile ratio obtained in the monoaddition reaction of hydrogen cyanide with 1,3-butadiene or the 1,3-butadiene-containing hydrocarbon mixture immediately after the end of the addition reaction (unconverted hydrogen cyanide no longer present) is at least 0.4:1. Advantageously, an isomerization additionally takes place at higher reaction temperatures and/or during longer reaction times in the presence of the novel catalysts, the 3-pentenitrile/2-methyl-3-butenitrile ratio obtained then generally being about 2:1, preferably about 5:1, in particular about 8:1.
- SUMM 2. Isomerization of the 2-methyl-3-butenitrile contained in these mixtures to give 3-pentenitrile and isomerization of the 3-pentenitrile thus formed and of the 3-pentenitrile already contained from step 1 to give various n-pentenitriles. A very high fraction of 3-pentenitrile or 4-pentenitrile and a very small

fraction of conjugated 2-pentenitrile and 2-methyl-2-butenitrile which may act as a catalyst poison should be formed.

- SUMM The novel catalysts based on phosphonite ligands are also advantageous for the positional and double bond isomerization in step 2 and/or the addition reaction of the second molecule of hydrogen cyanide in step 3.
- SUMM The present invention therefore furthermore relates to a process for the catalytic isomerization of branched aliphatic monoalkenenitriles having a nonconjugated C.dbd.C and C.tbd.N bond to give linear monoalkenenitriles, wherein the isomerization is carried out in the presence of a novel catalyst.
- SUMM Suitable branched aliphatic monoalkenenitriles are preferably acyclic, aliphatic, nonconjugated 2-alkyl-3-monoalkenenitriles and in particular 2-methyl-3-butenitrile. Mixtures of monoolefinic C.sub.5-monoalkenenitriles, as obtainable by the process, described above, for the catalytic hydrocyanation of butadiene or of 1,3-butadiene-containing hydrocarbon mixtures, are preferably used for the isomerization. Advantageously, the novel catalysts exhibit good activity with respect to the formation of linear monoalkene nitriles. The isomerization can, if desired, be effected in the presence of a conventional promoter, for example a Lewis acid, such as AlCl.sub.3 or ZnCl.sub.2. Advantageously, the novel catalysts generally permit isomerization without the addition of a promoter. The selectivity of the novel catalysts in the isomerization without the addition of a promoter is in general higher than that with the addition of a promoter. Furthermore, expensive removal of the promoter of the isomerization can be dispensed with. Thus, in principle only one catalyst circulation for hydrocyanation, isomerization and, if required, an addition reaction of a second molecule of hydrogen cyanide is required. Dispensing with the promoter and simplification of the process which is possible in principle generally permit a reduction of the costs compared with known processes.
- SUMM The present invention furthermore relates to a process for the preparation of adipodinitrile by catalytic hydrocyanation of linear monoolefinic C.sub.5-monoalkenenitriles, wherein the hydrocyanation is carried out in the presence of a novel catalyst. Advantageously, a mixture of monoolefinic C.sub.5-monoalkenenitriles which is obtainable by the novel process for the catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture and which, if required, was additionally subjected to working up and/or to isomerization by the novel isomerization process described above is used for the hydrocyanation. In a suitable embodiment of the novel process, the hydrocyanation of the monoolefinic C.sub.5-monoalkenenitriles is carried out in the presence of a promoter, for example a Lewis acid, such as AlCl.sub.3, ZnCl.sub.2, BF.sub.3, B(C.sub.6H.sub.5).sub.3, SnCl.sub.4, Sn(C.sub.6H.sub.5).sub.5).sub.3, etc.
- SUMM In a suitable embodiment of the novel process for the preparation of adipodinitrile, the catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture (Step 1) and the isomerization (Step 2) are carried out in the manner of a one-pot reaction without isolation of the hydrocyanation products. Hydrocyanation and isomerization can be carried out, for example, in one reactor, the reaction temperature being increased, if required, after the end of the hydrogen cyanide addition. Hydrocyanation and isomerization can also be carried out in separate reactors, where, for example, after the end of the monoaddition reaction of hydrogen cyanide in a first reactor, the catalyst-containing reaction mixture is

transferred, without isolation and working up, to a second reactor and is isomerized therein.

SUMM a) preparation of a mixture of monoolefinic C.sub.5-mononitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture,

SUMM b) catalytic isomerization of the mixture from a), and

SUMM c) catalytic hydrocyanation of the isomerized mixture from b), wherein the steps a), b) and c) are carried out in the presence of at least one novel catalyst and without isolation of the product or products from step a) and/or b).

SUMM The novel catalysts can be prepared simply and thus economically from readily obtainable intermediates, some of which are commercially available. Advantageously, they have high activity and good selectivity with respect to the monoadducts or isomerization products obtained in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures. In general, they have higher stability relative to hydrogen cyanide than conventional hydrocyanation catalysts and, in the hydrocyanation, an excess of hydrogen cyanide can also be added to said catalysts without resulting in marked deposition of inactive nickel(II) compounds, e.g. nickel(II) cyanide. In contrast to known hydrocyanation catalysts based on non-complex phosphine and phosphite ligands, the novel catalysts are therefore suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide in the reaction mixture can generally be effectively avoided but also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. Thus, the catalysts used according to the invention and the hydrocyanation processes based on them generally have higher catalyst recycling rates and longer catalyst on-stream times than known processes. This is advantageous not only for achieving better cost-efficiency but also from ecological points of view, since the nickel cyanide formed from the active catalyst with hydrogen cyanide is highly toxic and must be worked up or disposed of at high cost. Moreover, in the preparation of the novel catalysts, generally no excess or a smaller excess of ligand is required relative to the metal of subgroup VIII than in the case of conventional catalysts.

SUMM In addition to the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures, the catalysts of the formula I are generally suitable for all conventional hydrocyanation processes. In particular, the hydrocyanation of nonactivated olefins, for example of styrene and 3-pentenitrile, may be mentioned.

SUMM The catalysts which are described above and comprise chiral phosphonite ligands of the formula I are suitable for enantioselective hydrocyanation.

DETD 0.41 g (1.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0), 2.14 g of ligand I and 10 ml of toluene are initially taken under argon at room temperature in a glass autoclave and stirred for 10 minutes, the reaction batch acquiring a red-brown color. A mixture of 7.9 g (146 mmol) of 1,3-butadiene and 40 g of toluene is then added. The glass autoclave is tightly closed and the reaction mixture is heated to 70° C., an initial pressure of 1.2 bar being established. A mixture of 3.2 g (118 mmol) of freshly distilled hydrocyanic acid in 40 g of toluene is continuously metered in over a period of 90 minutes.

Thereafter, the pressure has fallen to 0.5 bar. The reaction is then completed in the course of a further 120 minutes at about 70° C. Toluene is used for washing the reaction discharge. The course of the reaction is monitored by pressure and temperature measurement.

DETD 0.41 g (1.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0), 2.9 g of ligand II and 10 g of toluene are initially taken under an argon atmosphere at room temperature in a glass autoclave and stirred for 10 minutes, the reaction batch acquiring a red-brown color. A mixture of 8.1 g (150 mmol) of 1,3-butadiene and 40 g of toluene is then added. The glass autoclave is tightly closed and the reaction mixture is heated to 90° C. A mixture of 4.0 g of freshly distilled hydrocyanic acid in 40 g of toluene is metered in continuously over a period of 90 minutes. After the end of the addition, the temperature is increased to 110° C. The course of the isomerization (ratio of 3-pentenitrile to 2-methyl-3-butenitrile) is investigated at regular intervals (0, 3, 6, 22 h) by means of GC analysis, as described in Example 1. The results are shown in Table 1.

DETD 0.72 g of ligand I, 15 ml of toluene and 0.14 g (0.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0) are initially taken under an argon atmosphere and stirred at room temperature for 45 minutes. The catalyst complex which forms is precipitated from the initially homogeneous solution. The volatile components are removed at highly superatmospheric pressure. 40.5 g (500 mmol) of 2-methyl-3-butenitrile are added to the remaining solid. The solution is heated to 110° C. The course of the reaction is investigated at regular intervals by means of a gas chromatograph. The product ratio after a reaction time of 300 minutes is shown in Table 2. All products and by-products shown there were assigned beforehand by means of gas chromatography, GC-MS, GC-MS-IR and NMR. All values are in GC percent by area.

DETD As demonstrated by Example 3, isomerization using the novel catalysts is also possible without the addition of a promoter.

DETD 0.39 g of ligand II, 8 ml of toluene and 0.07 g (0.25 mmol) of bis(1,5-cyclooctadienyl)nickel(0) are initially taken under an argon atmosphere and stirred at room temperature for 30 minutes. Some of the catalyst complex which forms is precipitated from the initially red homogeneous solution. The volatile components are removed at highly superatmospheric pressure. 20.2 g (250 mmol) of 2-methyl-3-butenitrile are added to the remaining solid. The solution is heated to 125° C. The course of the reaction is investigated at regular intervals by means of a gas chromatograph. The product ratio after a reaction time of 300 minutes is shown in Table 3. All products and by-products shown there were assigned beforehand by means of gas chromatography, GC-MS, GC-MS-IR and NMR. All values are in GC percent by area.

1. A catalyst composition comprising a complex of a metal of group VIII, and a bidentate phosphonite ligand of the formula I ##STR10## where A is a C.sub.2- to C.sub.7-alkylene bridge which may have 1, 2 or 3 double bonds and/or 1, 2 or 3 substituents which are selected from alkyl, cycloalkyl and aryl, it being possible for the aryl substituent additionally to carry 1, 2 or 3 substituents which are selected from alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxy carbonyl and cyano, and/or the C.sub.2- to C.sub.7-alkylene bridge may be interrupted by 1, 2 or 3 non-neighboring, unsubstituted or substituted heteroatoms, and/or the C.sub.2- to C.sub.7-alkylene bridge may be fused with one, two or three aryl and/or hetaryl groups, it being possible for the fused aryl and hetaryl groups each to carry 1, 2 or 3 substituents which are selected from alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl, halogen, trifluoromethyl, nitro, cyano, carboxyl, alkoxy carbonyl and NE.sup.1E.sup.2, where E.sup.1 and E.sup.2 are identical or different and are each alkyl, cycloalkyl or aryl, R.sup.1 and R.sup.1',

independently of one another, are each alkyl, cycloalkyl, aryl or hetaryl, each of which may carry 1, 2 or 3 substituents which are selected from alkyl, cycloalkyl and aryl, R.sup.2 and R.sup.2', independently of one another, are each alkyl, cycloalkyl, aryl or hetaryl, it being possible for the aryl and hetaryl groups each to carry 1, 2 or 3 substituents which are selected from alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl, halogen trifluoromethyl, nitro, cyano, carboxyl, alkoxycarbonyl and NE.sup.1E.sup.2, where E.sup.1 and E.sup.2 may have the abovementioned meanings, or a salt or mixture thereof.

2. The catalyst composition as claimed in claim 1, A being a radical of the formulae II.1 to II-5 ##STR11## where X is O, S or NR.sup.5, where R.sup.5 is alkyl, cycloalkyl or aryl, or X is a C.sub.1- to C.sub.3-alkylene bridge which may have a double bond and/or an alkyl, cycloalkyl or aryl substituent, wherein the aryl is optionally substituted by one, two or three substituents, which are selected from alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl and cyano, or X is a C.sub.2- or C.sub.3-alkylene bridge which is interrupted by O, S or NR.sup.5, and R.sup.3, R.sup.3', R.sup.3", R.sup.3'", R.sup.4, R.sup.4', R.sup.4" and R.sup.4'" independently of one another, are each hydrogen, alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl or cyano.

3. The catalyst composition as claimed in claim 1, R.sup.1 and R.sup.1', independently of one another, being alkyl or aryl.

4. The catalyst composition as claimed in claim 1, R.sup.2 and R.sup.2', independently of one another, each being phenyl substituents which may have one or two substituents which are selected from alkyl, alkoxy, halogen, trifluoromethyl, nitro, cyano, alkoxycarbonyl and carboxyl.

5. The catalyst composition as claimed in claim 1, the phosphonite ligand of the formula I being selected from ligands of the formulae Ia to Ic ##STR12## where, in the formula Ia, R.sup.3, R.sup.4, R.sup.7 and R.sup.8 have the following meanings:

R.sup.3 R.sup.4 R.sup.7 R.sup.8

H H H H

tert-butyl methyl H H

tert-butyl methoxy H H

H H methyl H

H H ethyl H

H H isopropyl H

H H tert-butyl H

H Cl H H

H CF.sub.3 H H

H H methyl methoxy in the formula Ib, R.sup.4, R.sup.7, R.sup.8 and R.sup.9 have the following meanings

R.sup.4 R.sup.7 R.sup.8 R.sup.9

H H H H

Cl H H H

methoxy H H H

H H H phenyl

H methyl H H

H methyl methoxy H

H methyl methoxy phenyl in the formula Ic, R.sup.7 and R.sup.8 have the following meanings:

R.sup.7 R.sup.8

H H  
methyl H  
ethyl H  
isopropyl H  
tert-butyl H  
methyl methoxy  
i-propyl H  
i-propyl methoxy  
H Cl  
H CF.sub.3

6. The catalyst composition as claimed in claim 1, which additionally has at least one further ligand selected from cyanide, halides, amines, carboxylates, acetylacetone, arylsulfonates, alkanesulfonates, hydride, CO, olefins, dienes, cycloolefins, nitriles, N-containing heterocycles, aromatics and heteroaromatics, ethers, PF.sub.3 and mono-, bi- and polydentate phosphine, phosphinite and phosphite ligands.

7. The catalyst composition as claimed in claim 1, the metal of group VIII being cobalt, rhodium, ruthenium, palladium or nickel.

9. A process for the preparation of a mixture of monoolefinic C.sub.5-mono nitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, wherein the hydrocyanation is carried out in the presence of a catalyst composition as claimed in claim 1.

10. A process for the catalytic isomerization of branched aliphatic monoalkenenitriles having a nonconjugated C.dbd.C and C.tbd.N bond to give linear monoalkenenitriles, wherein the isomerization is carried out in the presence of a catalyst composition as claimed in claim 1.

11. A process for the preparation of adipodinitrile by catalytic hydrocyanation of a linear monoolefinic C.sub.5-mono nitrile, wherein the hydrocyanation is carried out in the presence of a catalyst composition as claimed in claim 1.

12. A process for the preparation of adipodinitrile, comprising a) preparation of a mixture of monoolefinic C.sub.5-mono nitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, b) catalytic isomerization of the mixture from a), and c) catalytic hydrocyanation of the isomerized mixture from b), wherein the steps a), b) and c) are carried out in the presence of at least one catalyst composition as claimed in claim 1 and without isolation of the product or products from step a) and/or b).

13. A process for the hydrocyanation and/or positional and double-bond isomerization of olefins, wherein the hydrocyanation and/or positional and double-bond isomerization of olefins is carried out in the presence of a catalyst composition as claimed in claim 1.

14. The catalyst composition as claimed in claim 3, wherein R.sup.1 and R.sup.1', independently of one another, are selected from the group consisting of phenyl,

IT 74-90-6, Hydrocyanic acid, reactions  
 (hydrocyanation of butadiene; group VIII metal complex catalyst with  
 bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 106-99-0, 1,3-Butadiene, reactions  
 (hydrocyanation; group VIII metal complex catalyst with bidentate  
 phosphonite ligand and manufacture of alkenenitriles)

IT 4635-87-4P, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-  
 butenenitrile  
 (manufacture and isomerization; group VIII metal complex catalyst with  
 bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 74-90-6, Hydrocyanic acid, reactions  
 (hydrocyanation of butadiene; group VIII metal complex catalyst with  
 bidentate phosphonite ligand and manufacture of alkenenitriles)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, 1,3-Butadiene, reactions  
 (hydrocyanation; group VIII metal complex catalyst with bidentate  
 phosphonite ligand and manufacture of alkenenitriles)

RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenitrile  
 (manufacture and isomerization; group VIII metal complex catalyst with  
 bidentate phosphonite ligand and manufacture of alkenenitriles)

RN 4635-87-4 USPATFULL

CN 3-Pentenitrile (CA INDEX NAME)



L88 ANSWER 55 OF 60 USPATFULL on STN

ACCESSION . . .

HCl to produce the phosphorus-containing polymer, which is then contacted with  
 an aromatic diol. The composition can be used as catalyst, for  
 example, for converting an unsaturated organic compound to a nitrile and  
 isomerizing a nitrile.

CAS INDEXING IS AVAILABLE FOR. . .

AB . . . HCl to produce the phosphorus-containing polymer, which is then  
 contacted with an aromatic diol. The composition can be used as catalyst,



- for example, for converting an unsaturated organic compound to a nitrile and isomerizing a nitrile.
- SUMM [0001] This invention relates to a polymeric phosphite composition and polymeric phosphite catalyst composition that can be useful for a variety of catalytic processes, to a process for producing the composition, and to a process for using the composition in the hydrocyanation of. . .
- SUMM [0002] Phosphorus-based ligands are ubiquitous in catalysis, finding use for a number of commercially important chemical transformations. Phosphorus-based ligands commonly encountered in catalysis include phosphines and phosphites. Monophosphine and monophosphite ligands are compounds which contain a single phosphorus atom which serves as a. . .
- SUMM [0003] Two industrially important catalytic reactions using phosphorus ligands of particular importance are olefin hydrocyanation and isomerization of branched nitrites to linear nitrites. Phosphite ligands. . .
- SUMM [0004] Recovery of the ligand and catalyst is important for a successful process. Typical separation procedures to remove the product(s) from the catalyst and ligand involve extraction with an immiscible solvent or distillation. It is usually difficult to recover the catalyst and ligand quantitatively. For instance, distillation of a volatile product from a non-volatile catalyst results in thermal degradation of the catalyst. Similarly, extraction results in some loss of catalyst into the product phase. For extraction, one would like to be able to tune the solubility of the ligand and catalyst to disfavor solubility in the product phase. These ligands and metals are often very expensive and thus it is important. . .
- SUMM [0005] One method to solve the problem of catalyst and product separation is to attach the catalyst to an insoluble support. Examples of this approach have been previously described, and general references on this subject can be. . . Chemistry, Pergamon Press, 1982, Chapter 55; and Beller, M., Cornils, B., Frohning, C. D., Kohlpaintner, C. W., Journal of Molecular Catalysis A, 104, 1995, 17-85 and Macromol. Symp. 1994, 80, 241. Specifically, monophosphine and monophosphite ligands attached to solid supports are described in these references. Bisphosphine ligands have also been attached to solid supports and used for catalysis, as described in for example U.S. Pat. No. 5,432,289; J. Mol. Catal. A, 1996, 112,217; and J. Chem. Soc., Chem.. . .
- SUMM [0007] There is always a need to develop a composition that can be used as or in a catalyst with substantially reduced loss during a catalytic reaction or separation of product from the catalyst. An object of the present invention is, therefore, to provide such a composition and to provide processes for making and. . .
- SUMM . . . weight and degree of branching can control the solubility of the composition. Another advantage of the invention is that the catalyst produced by the composition can be substantially recovered by filtration. Other objects and advantages of the present invention will become. . .
- SUMM [0010] According to a second embodiment of the invention, a composition that can be used as a catalyst is provided, which comprises (1) composition disclosed in the first embodiment, (2) a Group VIII metal selected from Ni, Co,. . .
- SUMM . . . to a sixth embodiment of the invention, a process is provided. The process comprises contacting, in the presence of a catalyst disclosed in the second embodiment of the invention, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition. . .
- SUMM . . . According to a seventh embodiment of the invention, a process is provided. The process comprises contacting a nitrile with the

- catalyst disclosed in the second embodiment of the invention to produce linear 3-alkenenitrile.
- SUMM . . . skilled in the art. For example, the diacetal can be prepared by refluxing di(trimethylolpropane) with salicylaldehyde with oxalic acid as catalyst. For references for preparing acetal from acid catalyzed reaction of an aldehyde and an alcohol, see Tetrahedron, 1996, 14599; Tet. Lett., 1989, 1609; Tetrahedron, 1990, 3315. 1,3-bis(2-hydroxyphenoxy)propane was. . .
- SUMM . . . and degree of branching. For soluble polymeric system, separation can therefore be done by extraction. With insoluble polymeric systems, the catalyst can be placed in fixed beds or separated by filtration from a reaction mixture. Alternatively, the solubility of the polymer. . . reactants and insoluble in the products. Thus, the reaction can be carried out homogeneously to obtain high conversion. The polymeric catalyst can then be separated by easy means such as decantation or filtration.
- SUMM . . . the compositions disclosed above can be combined with a Group VIII metal and, optionally, a Lewis acid to produce a catalyst composition. The term "Group VIII" refers to the ACS version of the Periodic Table of the Elements, 67<sup>sup</sup>.th edition (1986-1987),. . .
- SUMM [0067] Generally, a Group VIII compound is combined with a polymer disclosed above to produce a desired catalyst. Among the Group VIII compounds, a nickel compound, a cobalt compound, or a palladium compound is preferred. A nickel compound. . .
- SUMM . . . metal aluminum hydrides, metal alkyls, Li, Na, K, or H.sub.2. Elemental nickel, preferably nickel powder, when combined with a halogenated catalyst, as described in U.S. Pat. No. 3,903,120, is also a suitable source of zero-valent nickel.
- SUMM . . . The amount of transition metal can be any amount so long as favorable results can be obtained with respect to catalyst activity and process economy, when used as a catalyst. In general, the molar ratio of phosphorus ligand to transition metal generally can be from about 1:1 to about 100:1,. . .
- SUMM . . . invention can further comprise one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter can be an inorganic or organometallic compound in which the promoter contains at least one element selected. . . alkyl or aryl group). U.S. Pat. No. 4,874,884 describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3, and (C.sub.6H.sub.5).sub.3SnX, where X=CF.sub.3SO.sub.3, CH.sub.3C.sub.6H.sub.5SO.sub.3, or (C.sub.6H.sub.5).sub.3BCN. The mole ratio of promoter. . .
- SUMM . . . compound conversions is provided. The process can comprise, consist essentially of, or consist of contacting, in the presence of a catalyst composition, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile wherein the catalyst composition can be the same as that disclosed in the second embodiment of the invention. The term "fluid" can be. . .
- SUMM . . . unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethylenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile,. . .
- SUMM . . . process can be carried out, for example, by charging a suitable vessel such as a reactor with an unsaturated compound, catalyst composition, and solvent, if any to form a reaction mixture. Hydrogen

- cyanide can be initially combined with other components to. . .
- SUMM [0099] Another suitable technique is to charge the vessel with the catalyst and the solvent to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.
- SUMM [0100] The molar ratio of unsaturated compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as 5:1 to 100,000:1, preferably 100:1 to 5,000:1, HCN to catalyst.
- SUMM . . . solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the unsaturated compound and the catalyst. Suitable solvents include hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile. . . .
- SUMM [0103] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular unsaturated compound being used and the desired rate. Normally, temperatures of from -25° C. to 200° . . .
- SUMM . . . with "cyanobutene"). Suitable unsaturated compounds include unsubstituted hydrocarbons as well as hydrocarbons substituted with groups, which do not attack the catalyst, such as cyano. These unsaturated compounds include, but are not limited to, monoethylenically unsaturated compounds containing from 2 to 30. . .
- SUMM . . . in the presence of one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter is the same as that disclosed above.
- SUMM . . . to the triple bond of the cyano group. Suitable starting 2-alkyl-3-monoalkenenitriles can also carry groups that do not attack the catalyst, for example, another cyano group. Preferably, the starting 2-alkyl-3-monoalkenenitriles contain from 5 to 8 carbon atoms, excluding any additional substitution. . . .
- SUMM . . . in the presence of a solvent or diluent. Any solvent or diluent that is inert to or nondestructive of the catalyst can be used, however. Suitable solvents include, but are not limited to, aliphatic or aromatic hydrocarbons (hexane, cyclohexane, benzene), ethers. . .
- SUMM [0123] A nonoxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used if desired at the expense of loss of a proportion of the catalyst through oxidation.
- SUMM . . . nonvolatile, whereas the 2-methyl-3-butenenitrile reactant and the linear pentenenitrile products are relatively volatile. Accordingly, in a continuous flow procedure, the catalyst can be a component of the flowing system in a completely liquid-phase operation. It can also be in a mobile. . .
- SUMM [0126] The molar ratio of 2-alkyl-3-monoalkenenitrile to catalyst is generally greater than 1:1, usually in the range from about 5:1 to 20,000:1, preferably 100:1 to 5,000:1, for a. . .
- DETD [0127] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following. . .
- DETD [0129] A catalyst solution was prepared by warming 0.1 g Fascat 4102 (butyltin tris(2-ethylhexanoate)) and 10 g of 1,6-hexanediol on the hot plate. . . Am. Chem. Soc., 1954, 76,296 and Tetrahedron Lett., 1990, 413), 2.6 g of 1,6-hexanediol and 1.75 g of warm catalyst solution was placed in a 25 ml microwave 1-neck rb (round bottom) flask connected to a distillation head and receiver. . .

DETD [0132] Preparation of catalyst: A catalyst solution was prepared by adding 0.039 g of Ni(COD).sub.2 (0.14 mmol) to 0.397 g of polyester 1 (0.42 mmol of bidentate. . .

DETD [0133] Hydrocyanation of butadiene: 74 µl of the above catalyst solution (0.0019 mmol Ni) were added to 2 reaction vials fitted with septum caps. The vials were cooled to -20°. . .

DETD [0134] Isomerization of 2-methyl-3-butene nitrile (2M3BN): 82 µl of the above catalyst solution (0.0021 mmol Ni) were added to 2 reaction vials fitted with septum caps. 130 µl of a cold solution. . .

DETD [0135] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): 116 µl of the above catalyst solution (0.0030 mmol Ni), and 13 µl of a solution of ZnCl.sub.2 in 3PN (0.0067 mmol ZnCl.sub.2) were added to. . .

DETD . . . (21 mmol) N,N'-dimethyl-1,6-hexanediamine, 30 g deionized water, and 10.9 g (21 mmol) diphenyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate. The reactor contents were purged with nitrogen.

DETD [0153] Preparation of catalyst: 0.059 g of branched polymer 1 was weighed into each of 3 reaction vials equipped with septum caps. 200 µl. . .

DETD [0154] Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 µl of a solution of butadiene in toluene (0.925 mmol. . .

DETD . . . (2M3BN): 130 µl of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and heated at 125° C. for 3.0 hours. The reaction mixture was then. . .

DETD [0156] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of the catalyst samples prepared above was cooled to -20° C. and 125 µl of a solution of HCN, t-3PN, and 2-ethoxyethyl ether. . .

DETD [0158] Preparation of catalyst: 0.056 g of branched polymer 2 was weighed into each of 3 reaction vials equipped with septum caps. 200 µl. . .

DETD [0159] Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 µl of a solution of butadiene in toluene (0.925 mmol. . .

DETD . . . (2M3BN): 130 µl of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and placed in a hot block reactor set at 125° C. The sample. . .

DETD [0161] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of that catalyst samples prepared above was cooled to -20° C. and 125 µl of a solution of HCN, t-3PN, and 2-ethoxyethyl ether. . .

DETD . . . 1-8 and one of aromatic diol A--E. Examples 7-9 and 13-14 illustrate the importance of control of polymer morphology on catalyst activity and selectivity. ##STR11##

## TABLE 1

Selectivity and activity of several catalysts comprising polymeric phosphite ligands in the hydrocyanation of butadiene and t-3 pentenenitrile, and the isomerization of 2-methyl-3-butenitrile

3PN hydrocyanation  
BD hydrocyanation. . .

CLM What is claimed is:  
42. A process comprising an unsaturated compound with a fluid comprising hydrogen cyanide in the presence of a catalyst composition recited in any of claims 18 to 21.

45. A process comprising (a) contacting a diolefinic compound, in the presence of a catalyst composition, with a fluid comprising hydrogen cyanide to produce a 2-alkyl-3-monoalkenenitrile; and (b) contacting said 2-alkyl-3-monoalkenenitrile with said catalyst composition wherein said catalyst composition is recited in claims 18-21.

48. A process comprising contacting a 2-alkyl-3-monoalkenenitrile with a catalyst composition recited in claims 18-21.

- IT 4635-87-4P, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, Butadiene, reactions 592-51-8, 4-Pentenitrile 818-57-5, Methyl 4-pentenoate 818-58-6, Methyl 3-pentenoate 818-59-7, Methyl 2-pentenoate  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- PI US 2001049431 A1 20011206 <--|  
US 6855799 B2 20050215|
- AB A polymeric composition, a process for producing the composition, and a process for using the composition in, for example, hydrocyanation or isomerization are disclosed. The composition comprises repeat units derived from (1) a carbonyl compound, a monomer, and phosphorochloridite; (2) phosphorus trichloride, a polyhydric alcohol, and an aromatic diol; or (3) combinations of (1) and (2) in which the monomer can be a polyhydric alcohol, an amine, combinations thereof. The composition can further comprise a Group VIII metal and optionally a Lewis acid. The composition can be produced by (1) contacting a carbonyl compound with the monomer to produce an intermediate and contacting the intermediate with phosphorochloridite; (2) contacting phosphorus trichloride with a second polyhydric alcohol under a condition sufficient to produce a phosphorus-containing polymer and contacting the phosphorus-containing polymer with an aromatic diol; or (3) contacting an N,N-dialkyl dichlorophosphoramidite with a second polyhydric alcohol to produce a polymer phosphoramidite, contacting the polymer phosphoramidite with an acid such as HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst, for example, for converting an unsaturated organic compound to a nitrile and isomerizing a nitrile.
- SUMM [0001] This invention relates to a polymeric phosphite composition and polymeric phosphite catalyst composition that can be useful for a variety of catalytic processes, to a process for producing the composition, and to a process for using the composition in the hydrocyanation of unsaturated organic compounds and the isomerization of unsaturated nitriles.
- SUMM [0002] Phosphorus-based ligands are ubiquitous in catalysis, finding use for a number of commercially important chemical transformations. Phosphorus-based ligands commonly encountered in catalysis include phosphines and phosphites. Monophosphine and monophosphite ligands are compounds which contain a single phosphorus atom which serves as a donor to a transition metal. Bisphosphine, bisphosphite, and bis(phosphorus) ligands in general, contain two phosphorus donor atoms and typically form cyclic chelate structures with transition metals.
- SUMM [0003] Two industrially important catalytic reactions using phosphorus ligands of particular importance are olefin hydrocyanation and isomerization of branched nitrites to linear nitrites. Phosphite ligands are particularly good ligands for both reactions. The hydrocyanation of

ethylenically unsaturated compounds using transition metal complexes with monodentate phosphite ligands is well documented in the prior art. See for example U.S. Pat. Nos. 3,496,215; 3,631,191; 3,655,723; 3,766,237; and 5,543,536. Bidentate phosphite ligands have also been shown to be particularly useful ligands in the hydrocyanation of activated ethylenically unsaturated compounds. See for example, Baker, M. J., and Pringle, P. G., J. Chem. Soc., Chem. Commun., 1292, 1991; Baker et al., J. Chem. Soc., Chem. Commun., 803, 1991; WO 93,03839; U.S. Pat. Nos. 5,512,696; 5,723,641; 5,688,986.

SUMM [0004] Recovery of the ligand and catalyst is important for a successful process. Typical separation procedures to remove the product(s) from the catalyst and ligand involve extraction with an immiscible solvent or distillation. It is usually difficult to recover the catalyst and ligand quantitatively. For instance, distillation of a volatile product from a non-volatile catalyst results in thermal degradation of the catalyst. Similarly, extraction results in some loss of catalyst into the product phase. For extraction, one would like to be able to tune the solubility of the ligand and catalyst to disfavor solubility in the product phase. These ligands and metals are often very expensive and thus it is important to keep such losses to a minimum for a commercially viable process.

SUMM [0005] One method to solve the problem of catalyst and product separation is to attach the catalyst to an insoluble support. Examples of this approach have been previously described, and general references on this subject can be found in "Supported Metal Complexes", D. Reidel Publishing, 1985, Acta Polymer., 1996, 47, 1; Comprehensive Organometallic Chemistry, Pergamon Press, 1982, Chapter 55; and Beller, M., Cornils, B., Frohning, C. D., Kohlpaintner, C. W., Journal of Molecular Catalysis A, 104, 1995, 17-85 and Macromol. Symp. 1994, 80, 241. Specifically, monophosphine and monophosphite ligands attached to solid supports are described in these references. Bisphosphine ligands have also been attached to solid supports and used for catalysis, as described in for example U.S. Pat. No. 5,432,289; J. Mol. Catal. A, 1996, 112,217; and J. Chem. Soc., Chem. Commun., 1996, 653. The solid support in these prior art examples can be organic, e.g., a polymer resin, or inorganic in nature.

SUMM [0007] There is always a need to develop a composition that can be used as or in a catalyst with substantially reduced loss during a catalytic reaction or separation of product from the catalyst. An object of the present invention is, therefore, to provide such a composition and to provide processes for making and for using the composition.

SUMM [0008] An advantage of the invention composition is that varying the molecular weight and degree of branching can control the solubility of the composition. Another advantage of the invention is that the catalyst produced by the composition can be substantially recovered by filtration. Other objects and advantages of the present invention will become apparent as the invention is more fully disclosed below.

SUMM [0010] According to a second embodiment of the invention, a composition that can be used as a catalyst is provided, which comprises (1) composition disclosed in the first embodiment, (2) a Group VIII metal selected from Ni, Co, Pd, and combinations of two or more thereof, and optionally (3) a Lewis acid.

SUMM [0014] According to a sixth embodiment of the invention, a process is

provided. The process comprises contacting, in the presence of a catalyst disclosed in the second embodiment of the invention, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile.

SUMM [0015] According to a seventh embodiment of the invention, a process is provided. The process comprises contacting a nitrile with the catalyst disclosed in the second embodiment of the invention to produce linear 3-alkenenitrile.

SUMM [0054] These polyhydric alcohols can be produced by those skilled in the art. For example, the diacetal can be prepared by refluxing di(trimethylolpropane) with salicylaldehyde with oxalic acid as catalyst. For references for preparing acetal from acid catalyzed reaction of an aldehyde and an alcohol, see Tetrahedron, 1996, 14599; Tet. Lett., 1989, 1609; Tetrahedron, 1990, 3315. 1,3-bis(2-hydroxyphenoxy)propane was prepared by a literature procedure, J. Org. Chem., 48, 1983, 4867. 4,4'-ethylidenebis(2,5-dimethylphenol); 4,4'-propylidenebis(2,5-dimethylphenol); 4,4'-benzylidenebis(2,5-dimethylphenol); and 4,4'-ethylidenebis(2-isopropyl-5-methylphenol) can be prepared according to Bull. Chem. Soc. Jpn., 62, 3603 (1989).

SUMM [0065] The solubilities of these composition or polymeric phosphite ligands disclosed above generally depend on the molecular weight of the polymer and degree of branching. For soluble polymeric system, separation can therefore be done by extraction. With insoluble polymeric systems, the catalyst can be placed in fixed beds or separated by filtration from a reaction mixture. Alternatively, the solubility of the polymer can be adjusted to be soluble in the reactants and insoluble in the products. Thus, the reaction can be carried out homogeneously to obtain high conversion. The polymeric catalyst can then be separated by easy means such as decantation or filtration.

SUMM [0066] According to the second embodiment of the invention, the compositions disclosed above can be combined with a Group VIII metal and, optionally, a Lewis acid to produce a catalyst composition. The term "Group VIII" refers to the ACS version of the Periodic Table of the Elements, 67<sup>sup</sup>.th edition (1986-1987), CRC Handbook of Chemistry and Physics, Press, Boca Raton, Fla. The term "Group VIII metal" used in the invention can also refer to Group VIII metal compound or Group VIII metal complex.

SUMM [0067] Generally, a Group VIII compound is combined with a polymer disclosed above to produce a desired catalyst. Among the Group VIII compounds, a nickel compound, a cobalt compound, or a palladium compound is preferred. A nickel compound is more preferred. A zero-valent nickel compound containing a ligand that can be displaced by the polymer is the most preferred source of Group VIII metal. Zero-valent nickel compounds can be prepared or generated according to means known in the art such as disclosed in U.S. Pat. Nos. 3,496,217; 3,631,191; 3,846,461; 3,847,959 and 3,903,120. Two such preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene) and Ni{P(O--o--C.sub.6H.sub.4CH.sub.3).sub.3}.sub.2 (C.sub.2H.sub.4), both of which are known in the art.

SUMM [0068] Alternatively, divalent nickel compounds can be combined with a reducing agent, to serve as a source of zero-valent nickel in the reaction. Suitable divalent nickel compounds include compounds of the formula NiY.sub.2 where Y is halide, carboxylate, or acetylacetonate. Suitable reducing agents include metal borohydrides, metal aluminum

hydrides, metal alkyls, Li, Na, K, or H.sub.2. Elemental nickel, preferably nickel powder, when combined with a halogenated catalyst, as described in U.S. Pat. No. 3,903,120, is also a suitable source of zero-valent nickel.

SUMM [0069] The amount of transition metal can be any amount so long as favorable results can be obtained with respect to catalyst activity and process economy, when used as a catalyst. In general, the molar ratio of phosphorus ligand to transition metal generally can be from about 1:1 to about 100:1, preferably from about 1:1 to about 20:1 (moles phosphorus per mole metal).

SUMM [0071] The composition of the second embodiment of the invention can further comprise one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter can be an inorganic or organometallic compound in which the promoter contains at least one element selected from scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhodium and tin. Examples include ZnBr.sub.2, ZnI.sub.2, ZnCl.sub.2, ZnSO.sub.4, CuCl.sub.2, CuCl, Cu(O.sub.3SCF.sub.3).sub.2, CoCl.sub.2, CoI.sub.2, FeI.sub.2, FeCl.sub.3, FeCl.sub.2, FeCl.sub.2(THF).sub.2, TiCl.sub.4(THF).sub.2, TiCl.sub.4, TiCl.sub.3, ClTi(OiPr).sub.3, MnCl.sub.2, SnCl.sub.3, AlCl.sub.3, (C.sub.8H.sub.17)AlCl.sub.2, (C.sub.8H.sub.17).sub.2AlCl, (iso-C.sub.4H.sub.9).sub.2AlCl, Ph.sub.2AlCl, PhAlCl.sub.2, ReCl.sub.5, ZrCl.sub.4, NbCl.sub.5, YCl.sub.3, CrCl.sub.2, MoCl.sub.5, YCl.sub.3, CdCl.sub.2, LaCl.sub.3, Er(O.sub.3SCF.sub.3).sub.3, Yb(O.sub.2CCF.sub.3).sub.3, SmCl.sub.3, B(C.sub.6H.sub.5).sub.3, TaCl.sub.5. Suitable promoters are further described in U.S. Pat. Nos. 3,496,217; 3,496,218 and 4,774,353. These include metal salts (such as ZnCl.sub.2, CoI.sub.2, and SnCl.sub.2), and organometallic compounds (such as RAlCl.sub.2, R.sub.3SnO.sub.3SCF.sub.3, and R.sub.3B, where R is an alkyl or aryl group). U.S. Pat. No. 4,874,884 describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6H.sub.5).sub.3, and (C.sub.6H.sub.5).sub.3SnX, where X=CF.sub.3SO.sub.3, CH.sub.3CO.sub.2, or (C.sub.6H.sub.5).sub.3BCN. The mole ratio of promoter to Group VIII metal can be in the range of from about 1:1 to about 1000:1, preferably about 1:16 to about 50:1.

SUMM [0093] According to the sixth embodiment of the invention, a process that can be used in organic compound conversions is provided. The process can comprise, consist essentially of, or consist of contacting, in the presence of a catalyst composition, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile wherein the catalyst composition can be the same as that disclosed in the second embodiment of the invention. The term "fluid" can be gas, liquid, or both. Any fluid containing about 1 to 100% HCN can be used.

SUMM [0097] The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethylenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol



and combinations of two or more thereof.

- SUMM [0098] The hydrocyanation process can be carried out, for example, by charging a suitable vessel such as a reactor with an unsaturated compound, catalyst composition, and solvent, if any to form a reaction mixture. Hydrogen cyanide can be initially combined with other components to form the mixture. However, it is preferred that HCN is added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the reaction. As an alternative, a cyanohydrin can be used as the source of HCN. See, for example, U.S. Pat. No. 3,655,723.
- SUMM [0099] Another suitable technique is to charge the vessel with the catalyst and the solvent to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.
- SUMM [0100] The molar ratio of unsaturated compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as 5:1 to 100,000:1, preferably 100:1 to 5,000:1, HCN to catalyst.
- SUMM [0102] The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the unsaturated compound and the catalyst. Suitable solvents include hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated compound to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in gas phase.
- SUMM [0103] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular unsaturated compound being used and the desired rate. Normally, temperatures of from -25° C. to 200° C. can be used, the range of 0° C. to 150° C. being preferred.
- SUMM [0109] Examples of the unsaturated compounds include, but are not limited to, unsaturated organic compounds containing from 2 to approximately 30 carbon atoms. 3-Pentenitrile and 4-pentenitrile are especially preferred. When nonconjugated acyclic aliphatic monoethylenically unsaturated compounds are used, up to about 10% by weight of the monoethylenically unsaturated compound can be present in the form of a conjugated isomer, which itself may undergo hydrocyanation. For example, when 3-pentenitrile is used, as much as 10% by weight thereof may be 2-pentenitrile. (As used herein, the term "pentenitrile" is intended to be identical with "cyanobutene"). Suitable unsaturated compounds include unsubstituted hydrocarbons as well as hydrocarbons substituted with groups, which do not attack the catalyst, such as cyano. These unsaturated compounds include, but are not limited to, monoethylenically unsaturated compounds containing from 2 to 30 carbons such as ethylene, propylene, butene-1, pentene-2, hexene-2, and combinations of two or more thereof; nonconjugated diethylenically unsaturated compounds such as allene, substituted compounds such as 3-pentenitrile, 4-pentenitrile, methyl pent-3-enoate, and combinations of two or more thereof; and ethylenically unsaturated compounds having perfluoroalkyl substituents such as, for

example, C.sub.zF.sub.2z+1, where z is an integer of up to 20. The monoethylenically unsaturated compounds can also be conjugated to an ester group such as methyl pent-2-enoate.

- SUMM [0112] The process of the invention can be carried out in the presence of one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter is the same as that disclosed above.
- SUMM [0119] For example, 2-alkyl-3-monoalkenenitrile used as the starting material in the isomerization of the invention can result from the hydrocyanation of a diolefin disclosed above or can come from any other available sources. The olefinic double bond in the 2-alkyl-3-monoalkenenitriles used as the starting materials in the isomerization of this invention cannot be conjugated to the triple bond of the cyano group. Suitable starting 2-alkyl-3-monoalkenenitriles can also carry groups that do not attack the catalyst, for example, another cyano group. Preferably, the starting 2-alkyl-3-monoalkenenitriles contain from 5 to 8 carbon atoms, excluding any additional substitution. 2-Methyl-3-butenitrile is especially important in the production of adiponitrile. Other representative nitriles include 2-ethyl-3-butenitrile and 2-propyl-3-butenitrile.
- SUMM [0122] The process can be carried out in the absence or in the presence of a solvent or diluent. Any solvent or diluent that is inert to or nondestructive of the catalyst can be used, however. Suitable solvents include, but are not limited to, aliphatic or aromatic hydrocarbons (hexane, cyclohexane, benzene), ethers (diethyl ether, tetrahydrofuran, dioxane, glycol dimethyl ether, anisole), esters (ethyl acetate, methyl benzoate, THF), nitrites (acetonitrile, benzonitrile), or combinations of two or more thereof.
- SUMM [0123] A nonoxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used if desired at the expense of loss of a proportion of the catalyst through oxidation.
- SUMM [0124] The nickel complex is essentially nonvolatile, whereas the 2-methyl-3-butenitrile reactant and the linear pentenenitrile products are relatively volatile. Accordingly, in a continuous flow procedure, the catalyst can be a component of the flowing system in a completely liquid-phase operation. It can also be in a mobile non-flowing liquid state in a semi-vapor phase operation, or it may be in a fixed-bed state in a conventional flowing vapor-phase operation.
- SUMM [0126] The molar ratio of 2-alkyl-3-monoalkenenitrile to catalyst is generally greater than 1:1, usually in the range from about 5:1 to 20,000:1, preferably 100:1 to 5,000:1, for a batch or continuous operation.
- DETD [0127] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.
- DETD [0129] A catalyst solution was prepared by warming 0.1 g Fascat 4102 (butyltin tris(2-ethylhexanoate)) and 10 g of 1,6-hexanediol on the hot plate in a small vial with a small magnet. The solution was kept warm. A mixture containing 5 g of dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-

3,3'-dicarboxylate (0.0123 mmoles; reference for preparation; see J. Am. Chem. Soc., 1954, 76,296 and Tetrahedron Lett., 1990, 413), 2.6 g of 1,6-hexanediol and 1.75 g of warm catalyst solution was placed in a 25 ml microwave 1-neck rb (round bottom) flask connected to a distillation head and receiver with a pre-calibrated heating mantle while stirring magnetically until methanol started to distill off (the temperature was about 180° C. at which temperature the dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate had all dissolved). The temperature was then increased until the 1,6-hexanediol started to reflux in the top of the flask (220° C.). The mixture was allowed to reflux for about an hour and then house vacuum was gradually applied. Full pump vacuum was then applied to distill off the excess 1,6-hexanediol. The pressure was lowered very slowly to 4 mm Hg over the next two hours in order to avoid bumping. The reaction mixture was then polymerized at 270° C. for 2 hours while distilling off most of the 1,6-hexanediol. After cooling, the reaction mixture was refluxed with 25 ml of acetone for three hours and then cooled and filtered. NMR indicated degree of polymerization to be 6.

DETD [0132] Preparation of catalyst: A catalyst solution was prepared by adding 0.039 g of Ni(COD).sub.2 (0.14 mmol) to 0.397 g of polyester 1 (0.42 mmol of bidentate phosphite equivalents; the unit formula weight of the polymers were determined based on the expected formula) in 4.568 g toluene.

DETD [0133] Hydrocyanation of butadiene: 74 µl of the above catalyst solution (0.0019 mmol Ni) were added to 2 reaction vials fitted with septum caps. The vials were cooled to -20° C. and 120 µl of a solution of HCN in valeronitrile (0.830 mmol HCN) and 280 µl of a solution of butadiene (BD) in toluene (0.925 mmol BD) were added to each vial. The vials were sealed and placed in a hot-block reactor set at 80° C. Samples were removed after 1.5 and 3 hours and quenched by cooling to -20° C. The reaction mixtures were then diluted in ethyl ether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 67.5 and 68.7% of the starting HCN had been converted to useful pentenenitriles (the 3-pentenenitrile to 2-methyl-3-butenenitrile ratio was 1.1) after 1.5 and 3 hours respectively.

DETD [0134] Isomerization of 2-methyl-3-butene nitrile (2M3BN): 82 µl of the above catalyst solution (0.0021 mmol Ni) were added to 2 reaction vials fitted with septum caps. 130 µl of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to each vial. The vials were sealed and placed in a hot block reactor set at 125° C. Samples were removed after 1.5 and 3.0 hrs, cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 3.88 after 1.5 hrs and 5.50 after 3 hours.

DETD [0135] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): 116 µl of the above catalyst solution (0.0030 mmol Ni), and 13 µl of a solution of ZnCl.sub.2 in 3PN (0.0067 mmol ZnCl.sub.2) were added to a vial fitted with a septum cap. The vial was cooled to -20° C. and 125 µl of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 35.3% of the starting pentenenitriles had been converted to dinitrile product (88.1% yield based on HCN.) The selectivity to the linear ADN isomer was 92.7%.

DETD [0142] 1. A 75-cc stainless steel autoclave equipped with a glass sleeve

was charged with 3.05 g (21 mmol) N,N'-dimethyl-1,6-hexanediamine, 30 g deionized water, and 10.9 g (21 mmol) diphenyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate. The reactor contents were purged with nitrogen.

- DETD [0153] Preparation of catalyst: 0.059 g of branched polymer 1 was weighed into each of 3 reaction vials equipped with septum caps. 200  $\mu$ l of THF were added to each vial and the sample shaken. 320  $\mu$ l of a freshly made solution containing 0.015 mmol Ni(COD).sub.2 in toluene were added to each vial.
- DETD [0154] Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to  $-20^{\circ}$  C. and 280  $\mu$ l of a solution of butadiene in toluene (0.925 mmol BD) and 120  $\mu$ l of a solution of HCN in valeronitrile (0.830 mmol HCN) were added to the vial. The vial was sealed and heated at  $80^{\circ}$  C. for 3 hours. After a quench by cooling to  $-20^{\circ}$  C., the reaction mixture was then diluted in ethylether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 71.7% of the starting HCN had been converted to useful pentenenitriles (ratio of 3PN/2M3BN was 1.36) after 3 hours.
- DETD [0155] Isomerization of 2-methyl-3-butene nitrile (2M3BN): 130  $\mu$ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and heated at  $125^{\circ}$  C. for 3.0 hours. The reaction mixture was then cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 0.47 after 3 hrs.
- DETD [0156] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of the catalyst samples prepared above was cooled to  $-20^{\circ}$  C. and 125  $\mu$ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. 13  $\mu$ l of a solution of ZnCl.sub.2 in 3PN (0.0067 mmol ZnCl.sub.2) were added to the vial. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 23.4% of the starting pentenenitriles had been converted to dinitrile product (64.6% yield based on HCN.) The selectivity to the linear ADN isomer was 91.8%.
- DETD [0158] Preparation of catalyst: 0.056 g of branched polymer 2 was weighed into each of 3 reaction vials equipped with septum caps. 200  $\mu$ l of THF were added to each vial and the sample shaken. 320  $\mu$ l of a freshly made solution of 39 mg Ni(COD).sub.2 in 2.79 g toluene (0.015 mmol Ni) were added to each vial.
- DETD [0159] Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to  $-20^{\circ}$  C. and 280  $\mu$ l of a solution of butadiene in toluene (0.925 mmol BD) and 120  $\mu$ l of a solution of HCN in valeronitrile (0.830 mmol HCN) were added to the vial. The vial was sealed and placed in a hot-block reactor set at  $80^{\circ}$  C. The sample was removed after 3 hours and quenched by cooling to  $-20^{\circ}$  C. The reaction mixture was then diluted in ethylether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 84.8% of the starting HCN had been converted to useful pentenenitriles (ratio of 3PN/2M3BN was 0.51) after 3 hours.
- DETD [0160] Isomerization of 2-methyl-3-butene nitrile (2M3BN): 130  $\mu$ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and placed in a hot block reactor set at  $125^{\circ}$  C. The sample was removed after 3.0 hours, cooled and diluted in ethyl ether.

The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 0.8 after 3 hrs.

DETD [0161] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of that catalyst samples prepared above was cooled to -20° C. and 125 µl of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. 13 µL of a solution of ZnCl<sub>2</sub>.sub.2 in 3PN (0.0067 mmol ZnCl<sub>2</sub>.sub.2) were added to the vial. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 1.8% of the starting pentenenitriles had been converted to dinitrile product (5.0% yield based on HCN). The selectivity to the linear ADN isomer was 90.0%.

DETD [0168] In the representative examples in Table 1 the polymeric phosphite was prepared from one of the polyhydric alcohol 1-8 and one of aromatic diol A--E. Examples 7-9 and 13-14 illustrate the importance of control of polymer morphology on catalyst activity and selectivity.

##STR11##

TABLE 1

Selectivity and activity of several catalysts comprising polymeric phosphite ligands in the hydrocyanation of butadiene and t-3 pentenenitrile, and the isomerization of 2-methyl-3-butenitrile

Example	Isomerization diol 3PN/2M3BN	bridge	BD hydrocyanation		3PN hydrocyanation Selectivity to		
			yield.sup.a)	3PN/2M3	yield.sup.a)	ADN	
7.sup.b, d) 1	11.66	A	29.5	0.9	66.5	88.8	
8.sup.c, e) 1	11.69	A	76.9	1.9	59.0	88.6	
9.sup.c, f) 1	26.39	A	77.1	8.2	63.0	89.7	
10.sup.c) 1		B	32.0	0.7	50.2	80.7	5.28
11.sup.c) 1		D	68.2	1.5	50.8	87.1	17.17
12.sup.c, g) 1	1.57	B	74.0	0.8	49.5	83.6	
13.sup.c, h) 1	2.82	E	70.1	1.0	67.0	88.4	
14.sup.c) 2		C	83.5	1.2	43.5	78.7	17.81
15.sup.c) 3		A	69.9	31.5	59.5	92.8	21.01
16.sup.c) 5		C	74.4	18.2	62.5	90.1	21.93
17.sup.c) 4		A	73.8	2.5	38.5	94.4	1.51
18.sup.c) 6		A	73.6	19.5	63.3	91.9	18.72
19.sup.c) 7		A	86.0	2.7	50.8	95.5	15.47
20.sup.c) 7		C	86.5	1.3	12.0	94.7	16.81
21.sup.c) 8		D	84.5	2.5	31.25	89.9	18.28

.sup.a)Yield in % based on HCN.

.sup.b)Hydrocyanation and isomerization procedure analogous to that in Example 1A.

.sup.c)Hydrocyanation and isomerization procedure analogous to that in Example 4A.

.sup.d) 770 mg 1 were added to 412 mg PCl<sub>3</sub>.sub.3 in a mixture of 30 ml toluene and 20 ml THF at -30° C. 800 mg NEt<sub>3</sub>.sub.3 in 20 ml toluene at -30° C. were added. Stirred 60 hrs. Added 363 mg A and 700 mg

NET.sub.3 in 10 ml THF. Product was isolated by filtration.

- .sup.e) 650 mg NET.sub.3 in 5 ml THF were added to 412 mg PCl.sub.3 and 769 mg 1 in 15 ml THF at -30° C. over a period of 10 minutes. 3 ml THF were added and the slurry cooled in a -30° C. freezer. 363 mg A and 650 mg NET.sub.3 were added, resulting in a gel. 15 ml THF were added and the solution filtered. Solids were washed with hot H.sub.2O, then with acetone, CH.sub.3CN and THF.
- .sup.f) 650 mg NET.sub.3 in 15 ml THF were cooled to -30° C. and added to 412 mg PCl.sub.3 and 769 mg 1 in 20 ml of THF at -30° C.. The slurry was cooled after the addition. 363 mg A and 650 mg NET.sub.3 were added. The solution was filtered and solids washed with THF. The polymer was THF soluble.
- .sup.g) 412 mg PCl.sub.3 and 769 mg 1 in 20 ml toluene and 20 ml THF were cooled to -30° C. in a freezer. 800 mg NET.sub.3 in 20 ml toluene were added and the mixture cooled to -30° C. 790 mg E and 700 mg NET.sub.3 were added. The mixture was filtered, washed with THF and the product recovered by removal of the solvent.
- .sup.h) 1.679 g 1 was dissolved in 17 g toluene. 900 mg of PCl.sub.3 were added. 5 g N(nBu).sub.3 in 8.7 g toluene were cooled to -30° C. and added to the mixture. 1.727 g E, 2.6 g N(nBu).sub.3, and 20 ml toluene were added and the mixture stirred. The product was isolated by addition of CH.sub.3CN, filtration and washing with CH.sub.3CN.

42. A process comprising an unsaturated compound with a fluid comprising hydrogen cyanide in the presence of a catalyst composition recited in any of claims 18 to 21.

45. A process comprising (a) contacting a diolefinic compound, in the presence of a catalyst composition, with a fluid comprising hydrogen cyanide to produce a 2-alkyl-3-monoalkenenitrile; and (b) contacting said 2-alkyl-3-monoalkenenitrile with said catalyst composition wherein said catalyst composition is recited in claims 18-21.

48. A process comprising contacting a 2-alkyl-3-monoalkenenitrile with a catalyst composition recited in claims 18-21.

- IT 4635-87-4F, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
Butadiene, reactions 592-51-8, 4-Pentenitrile 818-57-5, Methyl 4-pentenoate 818-58-6, Methyl 3-pentenoate 818-59-7, Methyl 2-pentenoate  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- IT 4635-87-4F, 3-Pentenitrile  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)
- RN 4635-87-4 USPATFULL
- CN 3-Pentenitrile (CA INDEX NAME)



- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,  
Butadiene, reactions

10/586490

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic  
compsd. and isomerization of unsatd. nitriles)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 56 OF 60 USPATFULL on STN

ACCESSION . . .

HCl to produce the phosphorus-containing polymer, which is then contacted with  
an aromatic diol. The composition can be used as catalyst, for  
example, for converting an unsaturated organic compound to a nitrile and  
isomerizing a nitrile.

CAS INDEXING IS AVAILABLE FOR. . .

AB . . . HCl to produce the phosphorus-containing polymer, which is then  
contacted with an aromatic diol. The composition can be used as catalyst,  
for example, for converting an unsaturated organic compound to a nitrile and  
isomerizing a nitrile.

SUMM This invention relates to a polymeric phosphite composition and  
polymeric phosphite catalyst composition that can be useful for a  
variety of catalytic processes, to a process for producing the  
composition, and to a process for using the composition in the  
hydrocyanation of. . .

SUMM Phosphorus-based ligands are ubiquitous in catalysis, finding use for  
a number of commercially important chemical transformations.  
Phosphorus-based ligands commonly encountered in catalysis include  
phosphines and phosphites. Monophosphine and monophosphite ligands are  
compounds which contain a single phosphorus atom which serves as a. . .

SUMM Two industrially important catalytic reactions using phosphorus  
ligands of particular importance are olefin hydrocyanation and  
isomerization of branched nitrites to linear nitrites. Phosphite  
ligands. . .

SUMM Recovery of the ligand and catalyst is important for a successful  
process. Typical separation procedures to remove the product(s) from the  
catalyst and ligand involve extraction with an immiscible solvent or  
distillation. It is usually difficult to recover the catalyst and  
ligand quantitatively. For instance, distillation of a volatile product  
from a non-volatile catalyst results in thermal degradation of the  
catalyst. Similarly, extraction results in some loss of catalyst  
into the product phase. For extraction, one would like to be able to  
tune the solubility of the ligand and catalyst to disfavor solubility  
in the product phase. These ligands and metals are often very expensive  
and thus it is important. . .

SUMM One method to solve the problem of catalyst and product separation is

to attach the catalyst to an insoluble support. Examples of this approach have been previously described, and general references on this subject can be . . . Chemistry, Pergamon Press, 1982, Chapter 55; and Beller, M., Cornils, B., Frohning, C. D., Kohlpaintner, C. W., Journal of Molecular Catalysis A, 104, 1995, 17-85 and Macromol. Symp. 1994, 80, 241. Specifically, monophosphine and monophosphite ligands attached to solid supports are described in these references. Bisphosphine ligands have also been attached to solid supports and used for catalysis, as described in for example U.S. Pat. No. 5,432,289; J. Mol. Catal. A, 1996, 112,217; and J. Chem. Soc., Chem. . . .

SUMM There is always a need to develop a composition that can be used as or in a catalyst with substantially reduced loss during a catalytic reaction or separation of product from the catalyst. An object of the present invention is, therefore, to provide such a composition and to provide processes for making and. . . .

SUMM . . . weight and degree of branching can control the solubility of the composition. Another advantage of the invention is that the catalyst produced by the composition can be substantially recovered by filtration. Other objects and advantages of the present invention will become. . . .

SUMM According to a second embodiment of the invention, a composition that can be used as a catalyst is provided, which comprises (1) composition disclosed in the first embodiment, (2) a Group VIII metal selected from Ni, Co,. . . .

SUMM . . . to a sixth embodiment of the invention, a process is provided. The process comprises contacting, in the presence of a catalyst disclosed in the second embodiment of the invention, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition. . . .

SUMM According to a seventh embodiment of the invention, a process is provided. The process comprises contacting a nitrile with the catalyst disclosed in the second embodiment of the invention to produce linear 3-alkenenitrile.

SUMM . . . skilled in the art. For example, the diacetal can be prepared by refluxing di(trimethylolpropane) with salicylaldehyde with oxalic acid as catalyst. For references for preparing acetal from acid catalyzed reaction of an aldehyde and an alcohol, see Tetrahedron, 1996, 14599; Tet. Lett., 1989, 1609; Tetrahedron, 1990,3315. 1,3-bis(2-hydroxyphenoxy)propane was prepared. . . .

SUMM . . . and degree of branching. For soluble polymeric system, separation can therefore be done by extraction. With insoluble polymeric systems, the catalyst can be placed in fixed beds or separated by filtration from a reaction mixture. Alternatively, the solubility of the polymer. . . reactants and insoluble in the products. Thus, the reaction can be carried out homogeneously to obtain high conversion. The polymeric catalyst can then be separated by easy means such as decantation or filtration.

SUMM . . . the compositions disclosed above can be combined with a Group VIII metal and, optionally, a Lewis acid to produce a catalyst composition. The term "Group VIII" refers to the ACS version of the Periodic Table of the Elements, 67.sup.th edition (1986-1987),. . . .

SUMM Generally, a Group VIII compound is combined with a polymer disclosed above to produce a desired catalyst. Among the Group VIII compounds, a nickel compound, a cobalt compound, or a palladium compound is preferred. A nickel compound. . . .

SUMM . . . metal aluminum hydrides, metal alkyls, Li, Na, K, or H.sub.2. Elemental nickel, preferably nickel powder, when combined with a halogenated catalyst, as described in U.S. Pat. No. 3,903,120, is also a suitable source of zero-valent nickel.

SUMM The amount of transition metal can be any amount so long as favorable



results can be obtained with respect to catalyst activity and process economy, when used as a catalyst. In general, the molar ratio of phosphorus ligand to transition metal generally can be from about 1:1 to about 100:1, . . .

SUMM . . . invention can further comprise one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter can be an inorganic or organometallic compound in which the promoter contains at least one element selected. . . alkyl or aryl group). U.S. Pat. No. 4,874,884 describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6 H.sub.5).sub.3, and (C.sub.6 H.sub.5).sub.3 SnX, where X.dbd.CF.sub.3 SO.sub.3, CH.sub.3 C.sub.6 H.sub.5 SO.sub.3, . . .

SUMM . . . compound conversions is provided. The process can comprise, consist essentially of, or consist of contacting, in the presence of a catalyst composition, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile wherein the catalyst composition can be the same as that disclosed in the second embodiment of the invention. The term "fluid" can be. . .

SUMM . . . unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethylenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile, . . .

SUMM . . . process can be carried out, for example, by charging a suitable vessel such as a reactor with an unsaturated compound, catalyst composition, and solvent, if any to form a reaction mixture. Hydrogen cyanide can be initially combined with other components to. . .

SUMM Another suitable technique is to charge the vessel with the catalyst and the solvent to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.

SUMM The molar ratio of unsaturated compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as 5:1 to 100,000:1, preferably 100:1 to 5,000:1, HCN to catalyst.

SUMM . . . solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the unsaturated compound and the catalyst. Suitable solvents include hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitrites such as acetonitrile, . . .

SUMM The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular unsaturated compound being used and the desired rate. Normally, temperatures of from -25° C. to 200°. . .

SUMM . . . with "cyanobutene"). Suitable unsaturated compounds include unsubstituted hydrocarbons as well as hydrocarbons substituted with groups, which do not attack the catalyst, such as cyano. These unsaturated compounds include, but are not limited to, monoethylenically unsaturated compounds containing from 2 to 30. . .

SUMM . . . in the presence of one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter is the same as that disclosed above.

SUMM . . . to the triple bond of the cyano group. Suitable starting 2-alkyl-3-monoalkenenitriles can also carry groups that do not attack

the catalyst, for example, another cyano group. Preferably, the starting 2-alkyl-3-monoalkenenitriles contain from 5 to 8 carbon atoms, excluding any additional substitution. . . .

SUMM . . . in the presence of a solvent or diluent Any solvent or diluent that is inert to or nondestructive of the catalyst can be used, however. Suitable solvents include, but are not limited to, aliphatic or aromatic hydrocarbons (hexane, cyclohexane, benzene), ethers. . . .

SUMM A nonoxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used if desired at the expense of loss of a proportion of the catalyst through oxidation. . . .

SUMM . . . nonvolatile, whereas the 2-methyl-3-butenenitrile reactant and the linear pentenenitrile products are relatively volatile. Accordingly, in a continuous flow procedure, the catalyst can be a component of the flowing system in a completely liquid-phase operation. It can also be in a mobile. . . .

SUMM The molar ratio of 2-alkyl-3-monoalkenenitrile to catalyst is generally greater than 1:1, usually in the range from about 5:1 to 20,000:1, preferably 100:1 to 5,000:1, for a. . . .

DETD The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following. . . .

DETD A catalyst solution was prepared by warming 0.1 g Fascat 4102 (butyltin tris(2-ethylhexanoate)) and 10 g of 1,6-hexanediol on the hot plate. . . . J. Am. Chem. Soc., 1954, 76,296 and Tetrahedron Lett., 1990, 413), 2.6 g of 1,6-hexanediol and 1.75 g of warm catalyst solution was placed in a 25 ml microwave 1-neck rb (round bottom) flask connected to a distillation head and receiver. . . .

DETD Preparation of catalyst: A catalyst solution was prepared by adding 0.039 g of Ni(COD).sub.2 (0.14 mmol) to 0.397 g of polyester1 (0.42 mmol of bidentate phosphite. . . .

DETD Hydrocyanation of butadiene: 74 µl of the above catalyst solution (0.0019 mmol Ni) were added to 2 reaction vials fitted with septum caps. The vials were cooled to -20°. . . .

DETD Isomerization of 2-methyl-3-butene nitrile (2M3BA): 82 µl of the above catalyst solution (0.0021 mmol Ni) were added to 2 reaction vials fitted with septum caps. 130 µl of a cold solution. . . .

DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): 116 µl of the above catalyst solution (0.0030 mmol Ni), and 13 µl of a solution of ZnCl.sub.2 in 3PN (0.0067 mmol ZnCl.sub.2) were added to. . . .

DETD . . . (21 mmol) N,N'-dimethyl-1,6-hexanediamine, 30 g deionized water, and 10.9 g (21 mmol) diphenyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate. The reactor contents were purged with nitrogen. . . .

DETD Preparation of catalyst. 0.059 g of branched polymer 1 was weighed into each of 3 reaction vials equipped with septum caps. 200 µl. . . .

DETD Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 µl of a solution of butadiene in toluene (0.925 mmol. . . .

DETD . . . (2M3BN): 130 µl of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and heated at 125° C. for 3.0 hours. The reaction mixture was then. . . .

DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of the catalyst samples prepared above was cooled to -20° C. and 125 µl of a solution of HCN, t-3PN, and 2-ethoxyethyl ether. . . .

DETD Preparation of catalyst: 0.056 g of branched polymer 2 was weighed

into each of 3 reaction vials equipped with septum caps. 200  $\mu$ l. .

DETD Hyarocyanation of butadiene: One of the catalyst samples prepared above was cooled to  $-20^{\circ}$  C. and 280  $\mu$ l of a solution of butadiene in toluene (0.925 mmol. . .

DETD . . . (2M3BN): 130  $\mu$ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and placed in a hot block reactor set at  $125^{\circ}$  C. The sample. . .

DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of that catalyst samples prepared above was cooled to  $-20^{\circ}$  C. and 125  $\mu$ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether. . .

DETD . . . 1-8 and one of aromatic diol A-E. Examples 7-9 and 13-14 illustrate the importance of control of polymer morphology on catalyst activity and selectivity.

DETD TABLE 1

Selectivity and activity of several catalysts comprising polymeric phosphite ligands in the hydrocyanation of butadiene and t-3 pentenenitrile, and the isomerization of 2-methyl-3-butenenitrile

	BD hydrocyanation	Selectivity. . .
IT 4635-87-4P, 3-Pentenenitrile	16529-56-9P, 2-Methyl-3-butenenitrile	
	(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)	
IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,	Butadiene, reactions 592-51-8, 4-Pentenenitrile 818-57-5, Methyl 4-pentenoate 818-58-6, Methyl 3-pentenoate 818-59-7, Methyl 2-pentenoate	
	(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)	
PI US 6284865	B1 20010904	<--
AB	A polymeric composition, a process for producing the composition, and a process for using the composition in, for example, hydrocyanation or isomerization are disclosed. The composition comprises repeat units derived from (1) a carbonyl compound, a monomer, and phosphorochloridite; (2) phosphorus trichloride, a polyhydric alcohol, and an aromatic diol; or (3) combinations of (1) and (2) in which the monomer can be a polyhydric alcohol, an amine, combinations thereof. The composition can further comprise a Group VIII metal and optionally a Lewis acid. The composition can be produced by (1) contacting a carbonyl compound with the monomer to produce an intermediate and contacting the intermediate with phosphorochloridite; (2) contacting phosphorus trichloride with a second polyhydric alcohol under a condition sufficient to produce a phosphorus-containing polymer and contacting the phosphorus-containing polymer with an aromatic diol; or (3) contacting an N,N-dialkyl dichlorophosphoramidite with a second polyhydric alcohol to produce a polymer phosphoramidite, contacting the polymer phosphoramidite with an acid such as HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst, for example, for converting an unsaturated organic compound to a nitrile and isomerizing a nitrile.	
SUMM	This invention relates to a polymeric phosphite composition and polymeric phosphite catalyst composition that can be useful for a variety of catalytic processes, to a process for producing the composition, and to a process for using the composition in the hydrocyanation of unsaturated organic compounds and the isomerization of unsaturated nitriles.	
SUMM	Phosphorus-based ligands are ubiquitous in catalysis, finding use for	

a number of commercially important chemical transformations. Phosphorus-based ligands commonly encountered in catalysis include phosphines and phosphites. Monophosphine and monophosphite ligands are compounds which contain a single phosphorus atom which serves as a donor to a transition metal. Bisphosphine, bisphosphite, and bisphosphorus ligands in general, contain two phosphorus donor atoms and typically form cyclic chelate structures with transition metals.

SUMM Two industrially important catalytic reactions using phosphorus ligands of particular importance are olefin hydrocyanation and isomerization of branched nitrites to linear nitrites. Phosphite ligands are particularly good ligands for both reactions. The hydrocyanation of ethylenically unsaturated compounds using transition metal complexes with monodentate phosphite ligands is well documented in the prior art. See for example U.S. Pat. Nos. 3,496,215; 3,631,191; 3,655,723; 3,766,237; and 5,543,536. Bidentate phosphite ligands have also been shown to be particularly useful ligands in the hydrocyanation of activated ethylenically unsaturated compounds. See for example, Baker, M. J., and Pringle, P. G., J. Chem. Soc., Chem. Commun., 1292, 1991; Baker et al., J. Chem. Soc., Chem. Commun., 803, 1991; WO 93,03839; U.S. Pat. Nos. 5,512,696; 5,723,641; 5,688,986.

SUMM Recovery of the ligand and catalyst is important for a successful process. Typical separation procedures to remove the product(s) from the catalyst and ligand involve extraction with an immiscible solvent or distillation. It is usually difficult to recover the catalyst and ligand quantitatively. For instance, distillation of a volatile product from a non-volatile catalyst results in thermal degradation of the catalyst. Similarly, extraction results in some loss of catalyst into the product phase. For extraction, one would like to be able to tune the solubility of the ligand and catalyst to disfavor solubility in the product phase. These ligands and metals are often very expensive and thus it is important to keep such losses to a minimum for a commercially viable process.

SUMM One method to solve the problem of catalyst and product separation is to attach the catalyst to an insoluble support. Examples of this approach have been previously described, and general references on this subject can be found in "Supported Metal Complexes", D. Reidel Publishing, 1985, Acta Polymer., 1996, 47,1; Comprehensive Organometallic Chemistry, Pergamon Press, 1982, Chapter 55; and Beller, M., Cornils, B., Frohning, C. D., Kohlpaintner, C. W., Journal of Molecular Catalysis A, 104, 1995, 17-85 and Macromol. Symp. 1994, 80, 241. Specifically, monophosphine and monophosphite ligands attached to solid supports are described in these references. Bisphosphine ligands have also been attached to solid supports and used for catalysis, as described in for example U.S. Pat. No. 5,432,289; J. Mol. Catal. A, 1996, 112,217; and J. Chem. Soc., Chem. Commun., 1996, 653. The solid support in these prior art examples can be organic, e.g., a polymer resin, or inorganic in nature.

SUMM There is always a need to develop a composition that can be used as or in a catalyst with substantially reduced loss during a catalytic reaction or separation of product from the catalyst. An object of the present invention is, therefore, to provide such a composition and to provide processes for making and for using the composition.

SUMM An advantage of the invention composition is that varying the molecular weight and degree of branching can control the solubility of the composition. Another advantage of the invention is that the catalyst

produced by the composition can be substantially recovered by filtration. Other objects and advantages of the present invention will become apparent as the invention is more fully disclosed below.

- SUMM According to a second embodiment of the invention, a composition that can be used as a catalyst is provided, which comprises (1) composition disclosed in the first embodiment, (2) a Group VIII metal selected from Ni, Co, Pd, and combinations of two or more thereof, and optionally (3) a Lewis acid.
- SUMM According to a sixth embodiment of the invention, a process is provided. The process comprises contacting, in the presence of a catalyst disclosed in the second embodiment of the invention, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile.
- SUMM According to a seventh embodiment of the invention, a process is provided. The process comprises contacting a nitrile with the catalyst disclosed in the second embodiment of the invention to produce linear 3-alkenenitrile.
- SUMM These polyhydric alcohols can be produced by those skilled in the art. For example, the diacetal can be prepared by refluxing di(trimethylolpropane) with salicylaldehyde with oxalic acid as catalyst. For references for preparing acetal from acid catalyzed reaction of an aldehyde and an alcohol, see Tetrahedron, 1996, 14599; Tet. Lett., 1989, 1609; Tetrahedron, 1990, 3315. 1,3-bis(2-hydroxyphenoxy)propane was prepared by a literature procedure, J. Org. Chem., 48, 1983, 4867. 4,4'-ethylidenebis(2,5-dimethylphenol); 4,4'-propylidenebis(2,5-dimethylphenol); 4,4'-benzylidenebis(2,5-dimethylphenol); and 4,4'-ethylidenebis(2-isopropyl-5-methylphenol) can be prepared according to Bull. Chem. Soc. Jpn., 62, 3603 (1989).
- SUMM The solubilities of these composition or polymeric phosphite ligands disclosed above generally depend on the molecular weight of the polymer and degree of branching. For soluble polymeric system, separation can therefore be done by extraction. With insoluble polymeric systems, the catalyst can be placed in fixed beds or separated by filtration from a reaction mixture. Alternatively, the solubility of the polymer can be adjusted to be soluble in the reactants and insoluble in the products. Thus, the reaction can be carried out homogeneously to obtain high conversion. The polymeric catalyst can then be separated by easy means such as decantation or filtration.
- SUMM According to the second embodiment of the invention, the compositions disclosed above can be combined with a Group VIII metal and, optionally, a Lewis acid to produce a catalyst composition. The term "Group VIII" refers to the ACS version of the Periodic Table of the Elements, 67<sup>sup</sup>.th edition (1986-1987), CRC Handbook of Chemistry and Physics, Press, Boca Raton, Fla. The term "Group VIII metal" used in the invention can also refer to Group VIII metal compound or Group VIII metal complex.
- SUMM Generally, a Group VIII compound is combined with a polymer disclosed above to produce a desired catalyst. Among the Group VIII compounds, a nickel compound, a cobalt compound, or a palladium compound is preferred. A nickel compound is more preferred. A zero-valent nickel compound containing a ligand that can be displaced by the polymer is the most preferred source of Group VIII metal. Zero-valent nickel compounds can be prepared or generated according to means known in the art such as

disclosed in U.S. Pat. Nos. 3,496,217; 3,631,191; 3,846,461; 3,847,959 and 3,903,120. Two such preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene) and Ni{P(O-o-C.sub.6 H.sub.4 CH.sub.3).sub.3 }.sub.2 (C.sub.2 H.sub.4), both of which are known in the art.

SUMM Alternatively, divalent nickel compounds can be combined with a reducing agent, to serve as a source of zero-valent nickel in the reaction. Suitable divalent nickel compounds include compounds of the formula NiY.sub.2 where Y is halide, carboxylate, or acetylacetonate. Suitable reducing agents include metal borohydrides, metal aluminum hydrides, metal alkyls, Li, Na, K, or H.sub.2. Elemental nickel, preferably nickel powder, when combined with a halogenated catalyst, as described in U.S. Pat. No. 3,903,120, is also a suitable source of zero-valent nickel.

SUMM The amount of transition metal can be any amount so long as favorable results can be obtained with respect to catalyst activity and process economy, when used as a catalyst. In general, the molar ratio of phosphorus ligand to transition metal generally can be from about 1:1 to about 100:1, preferably from about 1:1 to about 20:1 (moles phosphorus per mole metal).

SUMM The composition of the second embodiment of the invention can further comprise one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter can be an inorganic or organometallic compound in which the promoter contains at least one element selected from scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include ZnBr.sub.2, ZnI.sub.2, ZnCl.sub.2, ZnSO.sub.4, CuCl.sub.2, CuCl, Cu(O.sub.3 SCF.sub.3).sub.2, CoCl.sub.2, CoI2, FeI.sub.2, FeCl.sub.3, FeCl.sub.2, FeCl.sub.2 (THF).sub.2, TiCl.sub.4 (THF).sub.2, TiCl.sub.4, TiCl.sub.3, ClTi(OiPr).sub.3, MnCl.sub.2, ScCl.sub.3, AlCl.sub.3, (C.sub.8 H.sub.17)AlCl.sub.2, (C.sub.8 H.sub.17).sub.2 AlCl, (iso-C.sub.4 H.sub.9).sub.2 AlCl, Ph.sub.2 AlCl, PhAlCl.sub.2, ReCl.sub.5, ZrCl.sub.4, NbCl.sub.5, VCl.sub.3, CrCl.sub.2, MoCl.sub.5, YCl.sub.3, CdCl.sub.2, LaCl.sub.3, Er(O.sub.3 SCF3).sub.3, Yb(O.sub.2 CCF.sub.3).sub.3, SmCl.sub.3, B(C.sub.6 H.sub.5).sub.3, TaCl.sub.5. Suitable promoters are further described in U.S. Pat. Nos. 3,496,217; 3,496,218 and 4,774,353. These include metal salts (such as ZnCl.sub.2, CoI.sub.2, and SnCl.sub.2), and organometallic compounds (such as RAlCl.sub.2, R.sub.3 SnO.sub.3 SCF3).sub.3, and R.sub.3 B, where R is an alkyl or aryl group). U.S. Pat. No. 4,874,884 describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.sub.2, FeCl.sub.2, ZnCl.sub.2, B(C.sub.6 H.sub.5).sub.3, and (C.sub.6 H.sub.5).sub.3 SnX, where X is dbd, CF.sub.3 SO.sub.3, CH.sub.3 C.sub.6 H.sub.5 SO.sub.3, or (C.sub.6 H.sub.5).sub.3 BCN. The mole ratio of promoter to Group VIII metal can be in the range of from about 1:1 to about 1000:1, preferably about 1:16 to about 50:1.

SUMM According to the sixth embodiment of the invention, a process that can be used in organic compound conversions is provided. The process can comprise, consist essentially of, or consist of contacting, in the presence of a catalyst composition, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile wherein the catalyst composition can be the same as that disclosed in the second embodiment of the invention. The term "fluid" can be gas, liquid, or both. Any fluid containing about 1 to

100% HCN can be used.

- SUMM The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen, or phosphorus. Examples of these heteroatom-substituted ethylenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenitrile, 4-pentenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol and combinations of two or more thereof.
- SUMM The hydrocyanation process can be carried out, for example, by charging a suitable vessel such as a reactor with an unsaturated compound, catalyst composition, and solvent, if any to form a reaction mixture. Hydrogen cyanide can be initially combined with other components to form the mixture. However, it is preferred that HCN is added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the reaction. As an alternative, a cyanohydrin can be used as the source of HCN. See, for example, U.S. Pat. No. 3,655,723.
- SUMM Another suitable technique is to charge the vessel with the catalyst and the solvent to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.
- SUMM The molar ratio of unsaturated compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as 5:1 to 100,000:1, preferably 100:1 to 5,000:1, HCN to catalyst.
- SUMM The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the unsaturated compound and the catalyst. Suitable solvents include hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitrites such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated compound to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in gas phase.
- SUMM The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular unsaturated compound being used and the desired rate. Normally, temperatures of from -25° C. to 200° C. can be used, the range of 0° C. to 150° C. being preferred.
- SUMM Examples of the unsaturated compounds include, but are not limited to, unsaturated organic compounds containing from 2 to approximately 30 carbon atoms. 3-Pentenitrile and 4-pentenitrile are especially preferred. When nonconjugated acyclic aliphatic monoethylenically unsaturated compounds are used, up to about 10% by weight of the monoethylenically unsaturated compound can be present in the form of a conjugated isomer, which itself may undergo hydrocyanation. For example, when 3-pentenitrile is used, as much as 10% by weight thereof may be 2-pentenitrile. (As used herein, the term "pentenenitrile" is intended to be identical with "cyanobutene"). Suitable unsaturated compounds include unsubstituted hydrocarbons as well as hydrocarbons substituted

with groups, which do not attack the catalyst, such as cyano. These unsaturated compounds include, but are not limited to, monoethylenically unsaturated compounds containing from 2 to 30 carbons such as ethylene, propylene, butene-1, pentene-2, hexene-2, and combinations of two or more thereof; nonconjugated diethylenically unsaturated compounds such as allene, substituted compounds such as 3-pentenitrile, 4-pentenitrile, methyl pent-3-enoate, and combinations of two or more thereof; and ethylenically unsaturated compounds having perfluoroalkyl substituents such as, for example, C.sub.z F.sub.2z+1, where z is an integer of up to 20. The monoethylenically unsaturated compounds can also be conjugated to an ester group such as methyl pent-2-enoate.

- SUMM The process of the invention can be carried out in the presence of one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter is the same as that disclosed above.
- SUMM For example, 2-alkyl-3-monoalkenenitrile used as the starting material in the isomerization of the invention can result from the hydrocyanation of a diolefin disclosed above or can come from any other available sources. The olefinic double bond in the 2-alkyl-3-monoalkenenitriles used as the starting materials in the isomerization of this invention cannot be conjugated to the triple bond of the cyano group. Suitable starting 2-alkyl-3-monoalkenenitriles can also carry groups that do not attack the catalyst, for example, another cyano group. Preferably, the starting 2-alkyl-3-monoalkenenitriles contain from 5 to 8 carbon atoms, excluding any additional substitution. 2-Methyl-3-butenitrile is especially important in the production of adiponitrile. Other representative nitrites include 2-ethyl-3-butenitrile and 2-propyl-3-butenitrile.
- SUMM The process can be carried out in the absence or in the presence of a solvent or diluent. Any solvent or diluent that is inert to or nondestructive of the catalyst can be used, however. Suitable solvents include, but are not limited to, aliphatic or aromatic hydrocarbons (hexane, cyclohexane, benzene), ethers (diethyl ether, tetrahydrofuran, dioxane, glycol dimethyl ether, anisole), esters (ethyl acetate, methyl benzoate, THF), nitrites (acetonitrile, benzonitrile), or combinations of two or more thereof.
- SUMM A nonoxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used if desired at the expense of loss of a proportion of the catalyst through oxidation.
- SUMM The nickel complex is essentially nonvolatile, whereas the 2-methyl-3-butenitrile reactant and the linear pentenenitrile products are relatively volatile. Accordingly, in a continuous flow procedure, the catalyst can be a component of the flowing system in a completely liquid-phase operation. It can also be in a mobile nonflowing liquid state in a semi-vapor phase operation, or it may be in a fixed-bed state in a conventional flowing vapor-phase operation.
- SUMM The molar ratio of 2-alkyl-3-monoalkenenitrile to catalyst is generally greater than 1:1, usually in the range from about 5:1 to 20,000:1, preferably 100:1 to 5,000:1, for a batch or continuous operation.
- DETD The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts,



proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.

- DETD A catalyst solution was prepared by warming 0.1 g Fascat 4102 (butyltin tris(2-ethylhexanoate)) and 10 g of 1,6-hexanediol on the hot plate in a small vial with a small magnet. The solution was kept warm. A mixture containing 5 g of dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate (0.0123 mmoles; reference for preparation; see J. Am. Chem. Soc., 1954, 76, 296 and Tetrahedron Lett., 1990, 413), 2.6 g of 1,6-hexanediol and 1.75 g of warm catalyst solution was placed in a 25 ml microwave 1-neck rb (round bottom) flask connected to a distillation head and receiver with a pre-calibrated heating mantle while stirring magnetically until methanol started to distill off (the temperature was about 180° C. at which temperature the dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate had all dissolved). The temperature was then increased until the 1,6-hexanediol started to reflux in the top of the flask (220° C.). The mixture was allowed to reflux for about an hour and then house vacuum was gradually applied. Full pump vacuum was then applied to distill off the excess 1,6-hexanediol. The pressure was lowered very slowly to 4 mm Hg over the next two hours in order to avoid bumping. The reaction mixture was then polymerized at 270° C. for 2 hours while distilling off most of the 1,6-hexanediol. After cooling, the reaction mixture was refluxed with 25 ml of acetone for three hours and then cooled and filtered. NMR indicated degree of polymerization to be 6.
- DETD Preparation of catalyst: A catalyst solution was prepared by adding 0.039 g of Ni(COD).sub.2 (0.14 mmol) to 0.397 g of polyester 1 (0.42 mmol of bidentate phosphite equivalents; the unit formula weight of the polymers were determined based on the expected formula) in 4.568 g toluene.
- DETD Hydrocyanation of butadiene: 74 µl of the above catalyst solution (0.0019 mmol Ni) were added to 2 reaction vials fitted with septum caps. The vials were cooled to -20° C. and 120 µl of a solution of HCN in valeronitrile (0.830 mmol HCN) and 280 µl of a solution of butadiene (BD) in toluene (0.925 mmol BD) were added to each vial. The vials were sealed and placed in a hot-block reactor set at 80° C. Samples were removed after 1.5 and 3 hours and quenched by cooling to -20° C. The reaction mixtures were then diluted in ethyl ether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 67.5 and 68.7% of the starting HCN had been converted to useful pentenenitriles (the 3-pentenenitrile to 2-methyl-3-butenitrile ratio was 1.1) after 1.5 and 3 hours respectively.
- DETD Isomerization of 2-methyl-3-butene nitrile (2M3BA): 82 µl of the above catalyst solution (0.0021 mmol Ni) were added to 2 reaction vials fitted with septum caps. 130 µl of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to each vial. The vials were sealed and placed in a hot block reactor set at 125° C. Samples were removed after 1.5 and 3.0 hrs, cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 3.88 after 1.5 hrs and 5.50 after 3 hours.
- DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): 116 µl of the above catalyst solution (0.0030 mmol Ni), and 13 µl of a solution of ZnCl.sub.2 in 3PN (0.0067 mmol ZnCl.sub.2) were added to a vial fitted with a septum cap. The vial was cooled to -20° C. and 125 µl of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. The vial was sealed and set aside for 24

- hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 35.3% of the starting pentenenitriles had been converted to dinitrile product (88.1% yield based on HCN.) The selectivity to the linear ADN isomer was 92.7%.
- DETD 1. A 75-cc stainless steel autoclave equipped with a glass sleeve was charged with 3.05 g (21 mmol) N,N'-dimethyl-1,6-hexanediamine, 30 g deionized water, and 10.9 g (21 mmol) diphenyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate. The reactor contents were purged with nitrogen.
- DETD Preparation of catalyst. 0.059 g of branched polymer 1 was weighed into each of 3 reaction vials equipped with septum caps. 200  $\mu$ l of THF were added to each vial and the sample shaken. 320  $\mu$ l of a freshly made solution containing 0.015 mmol Ni(COD).sub.2 in toluene were added to each vial.
- DETD Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280  $\mu$ l of a solution of butadiene in toluene (0.925 mmol BD) and 120  $\mu$ l of a solution of HCN in valeronitrile (0.830 mmol HCN) were added to the vial. The vial was sealed and heated at 80° C. for 3 hours. After a quench by cooling to -20° C., the reaction mixture was then diluted in ethylether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 71.7% of the starting HCN had been converted to useful pentenenitriles (ratio of 3PN/2M3BN was 1.36) after 3 hours.
- DETD Isomerization of 2-methyl-3-butene nitrile (2M3BN): 130  $\mu$ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and heated at 125° C. for 3.0 hours. The reaction mixture was then cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 0.47 after 3 hrs.
- DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of the catalyst samples prepared above was cooled to -20° C. and 125  $\mu$ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. 13  $\mu$ l of a solution of ZnCl.sub.2 in 3PN (0.0067 mmol ZnCl.sub.2) were added to the vial. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 23.4% of the starting pentenenitriles had been converted to dinitrile product (64.6% yield based on HCN.) The selectivity to the linear ADN isomer was 91.8%.
- DETD Preparation of catalyst: 0.056 g of branched polymer 2 was weighed into each of 3 reaction vials equipped with septum caps. 200  $\mu$ l of THF were added to each vial and the sample shaken. 320  $\mu$ l of a freshly made solution of 39 mg Ni(COD).sub.2 in 2.79 g toluene (0.015 mmol Ni) were added to each vial.
- DETD Hyarocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280  $\mu$ l of a solution of butadiene in toluene (0.925 mmol BD) and 120  $\mu$ l of a solution of HCN in valeronitrile (0.830 mmol HCN) were added to the vial. The vial was sealed and placed in a hot-block reactor set at 80° C. The sample was removed after 3 hours and quenched by cooling to -20° C. The reaction mixture was then diluted in ethylether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 84.8% of the starting HCN had been converted to useful pentenenitriles (ratio of 3PN/2M3BN was 0.51) after

3 hours.

DETD Isomerization of 2-methyl-3-butene nitrile (2M3BN): 130  $\mu$ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and placed in a hot block reactor set at 125° C. The sample was removed after 3.0 hours, cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 0.8 after 3 hrs.

DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of that catalyst samples prepared above was cooled to -20° C. and 125  $\mu$ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. 13  $\mu$ L of a solution of ZnCl<sub>2</sub>.sub.2 in 3PN (0.0067 mmol ZnCl<sub>2</sub>.sub.2) were added to the vial. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 1.8% of the starting pentenenitriles had been converted to dinitrile product (5.0% yield based on HCN). The selectivity to the linear ADN isomer was 90.0%.

DETD In the representative examples in Table 1 the polymeric phosphite was prepared from one of the polyhydric alcohol 1-8 and one of aromatic diol A-E. Examples 7-9 and 13-14 illustrate the importance of control of polymer morphology on catalyst activity and selectivity.

DETD TABLE 1

Selectivity and activity of several catalysts comprising polymeric phosphite ligands in the hydrocyanation of butadiene and t-3 pentenenitrile, and the isomerization of 2-methyl-3-butenitrile

		3PN hydrocyanation					
Example	diol	bridge	BD hydrocyanation		Selectivity to		Isomerization ADN
			yield.sup.a)	3PN/2M3	yield.sup.a)		
3PN/2M3BN							
7.sup.b,d)	1	A	29.5	0.9	66.5	88.8	11.66
8.sup.c,e)	1	A	76.9	1.9	59.0	88.6	11.69
9.sup.c,f)	1	A	77.1	8.2	63.0	89.7	26.39
10.sup.c)	1	B	32.0	0.7	50.2	80.7	5.28
11.sup.c)	1	D	68.2	1.5	50.8	87.1	17.17
12.sup.c,g)	1	E	74.0	0.8	49.5	83.6	1.57
13.sup.c,h)	1	E	70.1	1.0	67.0	88.4	2.82
14.sup.c)	2	C	83.5	1.2	43.5	78.7	17.81
15.sup.c)	3	A	69.9	31.5	59.5	92.8	21.01
16.sup.c)	5	C	74.4	18.2	62.5	90.1	21.93
17.sup.c)	4	A	73.8	2.5	38.5	94.4	1.51
18.sup.c)	6	A	73.6	19.5	63.3	91.9	18.72
19.sup.c)	7	A	86.0	2.7	50.8	95.5	15.47
20.sup.c)	7	C	86.5	1.3	12.0	94.7	16.81
21.sup.c)	8	D	84.5	2.5	31.25	89.9	18.28

.sup.a) Yield in % based on HCN.

.sup.b) Hydrocyanation and isomerization procedure analogous to that in Example 1A.

.sup.c) Hydrocyanation and isomerization procedure analogous to that in Example 4A.

.sup.d) 770 mg 1 were added to 412 mg PCl<sub>3</sub>.sub.3 in a mixture of 30 ml toluene and 20 ml THF at -30° C. 800 mg NET<sub>3</sub>.sub.3 in 20 ml toluene at -30° C. were added. Stirred 60 hrs. Added 363 mg A and 700 mg NET<sub>3</sub>.sub.3 in 10 ml THF. Product was isolated by filtration.

.sup.e) 650 mg NET<sub>3</sub>.sub.3 in 5 ml THF were added to 412 mg PCl<sub>3</sub>.sub.3 and 769 mg 1 in 15 ml THF at -30° C. over a period of 10 minutes. 3 ml THF were added and the slurry cooled in a -30° C. freezer. 363 mg A and 650 mg NET<sub>3</sub>.sub.3 were added, resulting in a gel. 15 ml THF were added and

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the solution filtered. Solids were washed with hot H.sub.2 O, then with acetone, CH.sub.3 CN and THF.

.sup.f) 650 mg NET.sub.3 in 15 ml THF were cooled to -30° C. and added to 412 mg PCl.sub.3 and 769 mg 1 in 20 ml of THF at -30° C. The slurry was cooled after the addition. 363 mg A and 650 mg NET.sub.3 were added. The solution was filtered and solids washed with THF. The polymer was THF soluble.

.sup.g) 412 mg PCl.sub.3 and 769 mg 1 in 20 ml toluene and 20 ml THF were cooled to -30° C. in a freezer. 800 mg NET.sub.3 in 20 ml toluene were added and the mixture cooled to -30° C. 790 mg E and 700 mg NET.sub.3 were added. The mixture was filtered, washed with THF and the product recovered by removal of the solvent.

.sup.h) 1.679 g 1 was dissolved in 17 g toluene. 900 mg of PCl.sub.3 were added. 5 g N(nBu).sub.3 in 8.7 g toluene were cooled to -30° C. and added to the mixture. 1.727 g E, 2.6 g N(nBu).sub.3, and 20 ml toluene were added and the mixture stirred. The product was isolated by addition of CH.sub.3 CN, filtration and washing with CH.sub.3 CN.

IT 4635-87-4P, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 74-99-8, Hydrogen cyanide, reactions 106-99-0,  
Butadiene, reactions 592-51-8, 4-Pentenitrile 818-57-5, Methyl 4-pentenoate 818-58-6, Methyl 3-pentenoate 818-59-7, Methyl 2-pentenoate  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 4635-87-4P, 3-Pentenitrile  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

RN 4635-87-4 USPATFULL

CN 3-Pentenitrile (CA INDEX NAME)



IT 74-99-8, Hydrogen cyanide, reactions 106-99-0,  
Butadiene, reactions  
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

RN 74-99-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 57 OF 60 USPATFULL on STN

ACCESSION . . .

AB The disclosure is a process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation. CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The disclosure is a process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation.

SUMM . . . mononitriles in which the C.dbd.C bond and the C.tbd.N bond are not conjugated, to a process for their preparation by catalytic hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture, and to their use as intermediates for further processing to adiponitrile.

SUMM . . . way of removing acetylenes and allenes from diolefin-containing hydrocarbon mixtures consists in partly hydrogenating these mixtures in the presence of catalysts capable of differentiating between these classes of substances. For instance, U.S. Pat. No. 4,587,369 describes selective hydrogenation catalysts based on Pd on an alumina support.

SUMM U.S. Pat. No. 4,704,492 describes Cu/Pd catalysts useful as selective hydrogenation catalysts.

SUMM . . . for example 1,3-butadiene, while at the same time maximizing the removal of the acetylenes. U.S. Pat. No. 4,493,906 describes a catalyst based on finely divided copper on a  $\gamma$ -Al.sub.2 O.sub.3 support with which acetylene is removed virtually completely from a butadiene-containing. . .

SUMM . . . 150° C. and at atmospheric pressure. Nickel complexes with phosphine or phosphite ligands and metal salt promoters are used as catalysts. The abovementioned review contains no mention of a possible utility of an industrial C.sub.4 cut instead of pure 1,3-butadiene as. . .

SUMM Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 1, VCH Weinheim, pages 465 et seq., describes the heterogeneously and homogeneously catalyzed addition of hydrogen cyanide to olefins in general terms. Catalysts used are especially catalysts based on phosphine and phosphite complexes of nickel and palladium which permit a high product selectivity, improved conversions and shortened reaction times. Adiponitrile is prepared by hydrocyanation of butadiene using in the main nickel(0) phosphite catalysts, optionally in the presence of a Lewis acid as promoter. In general, the reaction can be divided into three steps: . . . the selectivity in respect of the linear 3-pentenitrile is within the range from about 70 to 90%, depending on the catalyst used. If this first reaction step is carried out in the absence of Lewis acids, generally no second addition of hydrogen cyanide takes place and the resulting product mixture can be subjected to an isomerization using the same catalyst systems as in the first reaction step, this time in the presence of a Lewis acid, for example ZnCl.sub.2, as. . . which the C,N triple bond is conjugated with the C,C double bond, inhibits the reaction, since it acts as a catalyst poison. The desired isomerization to 4-pentenitrile is only possible as a result

- of the fact that 3-pentenitrile is isomerized significantly. . .
- SUMM EP-A-0 274 401 describes a process for hydrocyanating pure butadiene using a nickel catalyst containing a mixture of phenyl and m,p-tolyl phosphite ligands.
- SUMM EP-A-315 551 describes a process for hydrocyanating pure dienes, for example 1,3-butadiene, 1,3-hexadiene, etc., by catalysis with a nickel(0) catalyst which contains an acid as promoter.
- SUMM . . . mixture of alkenes and alkanedienes by reacting the mixture with hydrogen cyanide in the presence of a nickel(0) complex as catalyst. The alkadienes react preferentially to form the corresponding nitriles and can be separated from the unconverted alkenes. Such an alkene-alkadiene. . .
- SUMM . . . completely from the nonconjugated products of value, 3-pentenitrile and 2-methyl-3-butenitrile, are not further hydrocyanable to adiponitrile and are also pronounced catalyst poisons.
- SUMM . . . in a first aspect a process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation.
- SUMM Components which give rise to catalyst poisons under catalytic hydrocyanation, especially alkynes, 1,2-dienes and mixtures thereof, are partially or completely removed from the hydrocarbon mixture.
- SUMM . . . which a C.dbd.C double bond is conjugated with the C.tbd.N bond. As mentioned above, it is known from Applied Homogeneous Catalysis with organometallic Compounds, Vol. 1, VCH Weinheim, page 479, that the conjugated 2-pentenitrile formed in the isomerization of 2-methyl-3-butenitrile and. . . form adiponitrile. It was found that the abovementioned conjugated nitriles obtained on hydrocyanating an untreated C.sub.4 cut also act as catalyst poisons for the first reaction step of adiponitrile production, the monoaddition of hydrogen cyanide. Direct consequences are a distinctly diminished catalytic activity of the homogeneous nickel catalyst, lower conversions and lower nickel retrieval rates in catalyst recovery. The disadvantages can be avoided, as is shown in the experimental part.
- SUMM . . . as well. These components are removed by subjecting the C.sub.4 cut prior to the addition of hydrogen cyanide to a catalytic partial hydrogenation. This partial hydrogenation takes place in the presence of a hydrogenation catalyst capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.
- SUMM Suitable catalysts for the selective hydrogenation are known from the prior art and include customary homogeneous and heterogeneous hydrogenation catalyst systems. The catalysts suitable for the process of the invention are preferably based on a transition metal of the 8th or 1st subgroup, preference being given to using catalysts based on Ni, Pd, Pt, Ru or Cu. Particular preference is given to using catalysts based on Cu or Pd.
- SUMM Suitable heterogeneous catalyst systems generally comprise one of the aforementioned transition metal compounds on an inert support. Suitable inorganic supports are the customary oxides, especially silicas and aluminas, aluminosilicates, zeolites, carbides, nitrides, etc. and mixtures thereof. Preferred supports are Al.sub.2 O.sub.3, SiO.sub.2 and mixtures thereof. The heterogeneous catalysts used in the process of the invention are in particular those described in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are all fully incorporated herein by reference. Further suitable Cu-based catalyst systems are marketed by Dow Chemical as KLP catalyst.
- SUMM a) feeding the partly hydrogenated C.sub.4 cut, hydrogen cyanide and

- hydrocyanation catalyst into a reactor,
- SUMM e) working up the liquid and solid reactor effluent by distillation and recycling the recovered catalyst into the reactor.
- SUMM The three components of the reaction mixture, hydrogen cyanide, partly hydrogenated C.sub.4 cut and catalyst, are generally fed in separate feeds at the rate of their respective consumption. If instead of a homogeneous catalyst, which can be introduced into the reactor for example separately as a solution in a suitable solvent or together with one of the other feeds, a heterogeneous catalyst is used, the latter can also be preinstalled in the reactor in a suitable form.
- SUMM . . . effluent is subjected to a distillative workup to isolate the desired products 3-pentenitrile and 2-methyl-3-butenitrile and also to recover the catalyst present. The recovered active catalyst is recycled into the reactor.
- SUMM a) filling a pressure-resistant reactor with the partly hydrogenated C.sub.4 cut, hydrogen cyanide and a hydrocyanation catalyst and optionally a solvent,
- SUMM The pressure-resistant reactor is charged with the partly hydrogenated C.sub.4 cut, hydrogen cyanide, a hydrocyanation catalyst and optionally a solvent before commencement of the reaction. Examples of suitable solvents are aromatic hydrocarbons, such as toluene and. . .
- SUMM . . . extraction and the distillative workup of the remaining reaction mixture to remove the products of value and recover still active catalyst.
- SUMM Suitable catalysts for the hydrocyanation are known from the prior art and include heterogeneous and preferably homogeneous catalyst systems. In general, catalysts suitable for the process of the invention are based on a transition metal of the 8th subgroup and optionally comprise a metal salt as promoter. The catalyst system used for the monoaddition of hydrogen cyanide preferably contains no addition of promoter.
- SUMM The process of the invention is preferably carried out using at least one homogeneous catalyst selected from salts or complexes of nickel. Of particular suitability are Ni(0) complexes with phosphine, phosphinite, phosphonite or preferably phosphite. . .
- SUMM The aforementioned catalysts can be used combined with a promoter, if desired. The promoter used is preferably a Lewis acid, for example AlCl<sub>3</sub>.sub.3 or ZnCl<sub>2</sub>.sub.2. The catalysts used for the monoaddition of hydrogen cyanide preferably contain no addition of a promoter.
- SUMM . . . to form various n-pentenitriles. The proportion of 3-pentenitrile formed should be as high as possible and the proportion of conjugated, catalyst-poisoning 2-pentenitrile and 2-methyl-2-butenitrile should be as low as possible.
- SUMM The nickel phosphite catalysts preferred for the novel preparation of monoolefinic nitriles in step 1 are advantageously also suitable for the position and double. . .
- SUMM . . . C.sub.4 cut pretreated according to the invention. Since the continuous process is carried out with recycling of the active nickel catalyst, and the catalyst is added to the reaction mixture only in small amounts, even a slight hydrogen cyanide excess due to incomplete conversion. . . adverse effect on the nickel balance of the reaction. Thus, the continuous process of the invention surprisingly has a higher catalyst recycling rate and so longer catalyst on-stream times than known processes. This is also relevant from ecological aspects, since the nickel cyanide formed from the active catalyst and hydrogen cyanide is highly toxic and has to be expensively worked up or disposed of.
- SUMM . . . which are isomerizable to 4-pentenitrile, such as 3-pentenitrile and 2-methyl-3-butenitrile. Furthermore, the proportion of conjugated 2-pentenitrile, which acts as a catalyst

- poison, is low and is preferably below 1% by weight, especially within the range from about 0.1 to 0.2% by. . .
- SUMM . . . form products having a C,C double bond conjugated with the nitrile function. Owing to the effect of these compounds as catalyst poisons, the nickel retrieval rates and the catalyst on-stream times are lower than in the process of the invention. Lower catalyst activities lead to lower conversions.
- SUMM . . . 1,3-butadiene-containing hydrocarbon mixture which additionally includes at least one alkyne and/or 1,2-diene with hydrogen in the presence of a hydrogenation catalyst.
- SUMM The present invention further provides a process for preparing adiponitrile, which comprises catalytically hydrocyanating a C.sub.5 mononitrile mixture prepared as described above, optionally after further workup or isomerization.
- DETD Catalyst Composition
- DETD Partly hydrogenated C.sub.4 cut, catalyst solution and hydrogen cyanide are introduced into a two stage stirred tank battery (pressure: 15 bar, temperature of reactor 1: . . . scrubbing tower. Liquid/solid effluents are analyzed, worked up by distillation to remove the products of value and recover still active catalyst, and the products thus obtained are again analyzed. The HCN conversions are determined by volumetric analysis of the reactor solutions from the two reactors. The nickel retrieval rate (recovery of active catalyst) is determined by means of elemental analysis.
- DETD An unhydrogenated hydrocarbon mixture of the above-specified composition is reacted similarly to Example 1, except that the catalyst feed is raised from 2.72 mmol/h to 4.85 mmol/h. The results are likewise reproduced in Table 1.
- DETD . . . the deficient component should have increased with increasing amount of excess component. Comparative Example 2, which utilizes a distinctly higher catalyst content, still does not match the results of Example 1.
- DETD 4.7 g of catalyst composition containing:
- DETD . . . 20.3 g of partially hydrogenated C.sub.4 cut (corresponding to 7.9 g (0.14 mol) of 1,3-butadiene), 2.75 g of a mixed catalyst (composition: 0.69 g (0.468 mmol) of tetrakis(tri-m/p-tolylphosphite)nickel(0), 1.65 g (4.68 mmol) of tri-m/p-tolylphosphite and 0.41 g 3-pentene nitrile) and 40. . .
- CLM What is claimed is:
1. A process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, wherein the hydrocarbon mixture is reacted with hydrogen in the presence of a hydrogenation catalyst capable of hydrogenating alkynes and 1,2-dienes with high selectivity without significantly diminishing the 1,3-butadiene content in order to remove alkynes, . . . and mixtures thereof partially or completely so that the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation is diminished and then subjecting the resulting mixture to catalytic hydrocyanation.
  5. The process of claim 1, wherein the hydrocyanation catalyst catalyzes the position isomerization and double bond isomerization of the hydrocarbon mixture and/or of the nitriles as well as the hydrogen. . .
  7. A process for preparing adiponitrile, which comprises catalytically hydrocyanating a C.sub.5 mononitrile mixture prepared as claimed in any of claims 1 to 6, optionally after further workup or. . .
- IT 106-99-0, Butadiene, reactions  
(hydrocyanation in purified C4 fractions)



IT 4635-87-4P, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile

(monoolefinic C5 mononitrile production and use)

IT 74-90-8, Hydrocyanic acid, reactions (reaction with butadiene)

PI US 6197992 B1 20010306  
WO 9827054 19980625

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AB The disclosure is a process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation. |

SUMM The present invention relates to monoolefinic C.sub.5 mononitriles in which the C.dbd.C bond and the C.tbd.N bond are not conjugated, to a process for their preparation by catalytic hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture, and to their use as intermediates for further processing to adiponitrile.

SUMM One way of removing acetylenes and allenes from diolefin-containing hydrocarbon mixtures consists in partly hydrogenating these mixtures in the presence of catalysts capable of differentiating between these classes of substances. For instance, U.S. Pat. No. 4,587,369 describes selective hydrogenation catalysts based on Pd on an alumina support.

SUMM U.S. Pat. No. 4,704,492 describes Cu/Pd catalysts useful as selective hydrogenation catalysts.

SUMM For certain uses of the hydrocarbon mixture, it is desirable to minimize the loss of diolefin, for example 1,3-butadiene, while at the same time maximizing the removal of the acetylenes. U.S. Pat. No. 4,493,906 describes a catalyst based on finely divided copper on a  $\gamma$ -Al.sub.2 O.sub.3 support with which acetylene is removed virtually completely from a butadiene-containing mixture and the butadiene loss is in the region of not more than 1%.

SUMM The last process produces in a first stage, by monoaddition, a mixture of isomeric pentenenitriles and methylbutenenitriles, which, in a second stage, is isomerized to predominantly 3- and 4-pentenitrile. Subsequently, in a third stage, the adiponitrile is formed by anti-Markovnikov hydrogen cyanide addition to 4-pentenitrile. The reaction takes place in the liquid phase in a solvent, for example tetrahydrofuran, at a temperature within the range from 30 to 150° C. and at atmospheric pressure. Nickel complexes with phosphine or phosphite ligands and metal salt promoters are used as catalysts. The abovementioned review contains no mention of a possible utility of an industrial C.sub.4 cut instead of pure 1,3-butadiene as reactant.

SUMM Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 1, VCH Weinheim, pages 465 et seq., describes the heterogeneously and homogeneously catalyzed addition of hydrogen cyanide to olefins in general terms. Catalysts used are especially catalysts based on phosphine and phosphite complexes of nickel and palladium which permit a high product selectivity, improved conversions and shortened reaction times. Adiponitrile is prepared by hydrocyanation of butadiene using in the main nickel(0) phosphite catalysts, optionally in the presence of a Lewis acid as promoter. In general, the reaction can be divided into three steps: 1. synthesis of mononitriles by hydrocyanation of 1,3-butadiene; 2. isomerization; 3. synthesis of dinitriles. The

monoaddition product is an isomeric mixture of 3-pentenitrile and 2-methyl-3-butenitrile, and the selectivity in respect of the linear 3-pentenitrile is within the range from about 70 to 90%, depending on the catalyst used. If this first reaction step is carried out in the absence of Lewis acids, generally no second addition of hydrogen cyanide takes place and the resulting product mixture can be subjected to an isomerization using the same catalyst systems as in the first reaction step, this time in the presence of a Lewis acid, for example  $\text{ZnCl}_2$ , as promoter. The 2-methyl-3-butenitrile isomerizes to 3-pentenitrile on the one hand, and 3-pentenitrile isomerizes to the various n-cyanonitriles on the other. The cited publication mentions that the thermodynamically most stable isomer, 2-pentenitrile, in which the C,N triple bond is conjugated with the C,C double bond, inhibits the reaction, since it acts as a catalyst poison. The desired isomerization to 4-pentenitrile is only possible as a result of the fact that 3-pentenitrile is isomerized significantly more rapidly to 4-pentenitrile than to 2-pentenitrile.

- SUMM EP-A-0 274 401 describes a process for hydrocyanating pure butadiene using a nickel catalyst containing a mixture of phenyl and m,p-tolyl phosphite ligands.
- SUMM EP-A-315 551 describes a process for hydrocyanating pure dienes, for example 1,3-butadiene, 1,3-hexadiene, etc., by catalysis with a nickel(0) catalyst which contains an acid as promoter.
- SUMM U.S. Pat. No. 4,434,316 describes a process for removing the alkenes from a mixture of alkenes and alkanedienes by reacting the mixture with hydrogen cyanide in the presence of a nickel(0) complex as catalyst. The alkadienes react preferentially to form the corresponding nitriles and can be separated from the unconverted alkenes. Such an alkene-alkadiene separation is necessary for example in industrial processes for the production of dinitriles in order that the alkenes, which cannot form dinitriles, can be separated from the alkadienes. The process described is suitable for separating alkenes having 2 to 5 carbon atoms, for example ethylene, propylene, butenes and propenes from alkadienes having 3 to 8 carbon atoms, for example propadiene, butadiene, pentadiene, hexadiene and octadiene. The presence of acetylenically and ethylenically-acetylenically unsaturated hydrocarbons is not considered disadvantageous for the separation process described. The reference does not mention the possibility of hydrocyanating a 1,3-butadiene-containing hydrocarbon mixture and especially a C.sub.4 cut from petroleum refineries to produce C.sub.5 monoolefin mixtures having a nitrile function.
- SUMM However, the prior art processes for hydrocyanating 1,3-butadiene-containing hydrocarbon mixtures have the disadvantage that conjugated butenenitriles and/or pentenenitriles are obtained as unwanted by-products. These conjugated butenenitriles and/or pentenenitriles are impossible to separate completely from the nonconjugated products of value, 3-pentenitrile and 2-methyl-3-butenitrile, are not further hydrocyanable to adiponitrile and are also pronounced catalyst poisons.
- SUMM The present invention accordingly provides in a first aspect a process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation.

- SUMM Components which give rise to catalyst poisons under catalytic hydrocyanation, especially alkynes, 1,2-dienes and mixtures thereof, are partially or completely removed from the hydrocarbon mixture.
- SUMM Especially the hydrocyanation of a C.sub.4 cut which is not completely free from alkynes, for example propyne or butyne, from 1,2-dienes, for example propadiene, and from alkenines, for example vinylacetylene, affords products in which a C.dbd.C double bond is conjugated with the C.tbd.N bond. As mentioned above, it is known from Applied Homogeneous Catalysis with organometallic Compounds, Vol. 1, VCH Weinheim, page 479, that the conjugated 2-pentenitrile formed in the isomerization of 2-methyl-3-butenitrile and 3-pentenitrile acts as a reaction inhibitor for the second addition of hydrogen cyanide to form adiponitrile. It was found that the abovementioned conjugated nitriles obtained on hydrocyanating an untreated C.sub.4 cut also act as catalyst poisons for the first reaction step of adiponitrile production, the monoaddition of hydrogen cyanide. Direct consequences are a distinctly diminished catalytic activity of the homogeneous nickel catalyst, lower conversions and lower nickel retrieval rates in catalyst recovery. The disadvantages can be avoided, as is shown in the experimental part.
- SUMM The production of monoolefinic C.sub.5 mononitriles according to the process of the invention is preferably carried out using an industrially produced hydrocarbon mixture having a high proportion of 1,3-butadiene. An example of an industrially produced hydrocarbon mixture having a high proportion of 1,3-butadiene is the C.sub.4 cut which is obtained in petroleum processing by steam cracking of naphtha and which as a consequence of its method of production always contains alkynes and 1,2-dienes as well. These components are removed by subjecting the C.sub.4 cut prior to the addition of hydrogen cyanide to a catalytic partial hydrogenation. This partial hydrogenation takes place in the presence of a hydrogenation catalyst capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.
- SUMM Suitable catalysts for the selective hydrogenation are known from the prior art and include customary homogeneous and heterogeneous hydrogenation catalyst systems. The catalysts suitable for the process of the invention are preferably based on a transition metal of the 8th or 1st subgroup, preference being given to using catalysts based on Ni, Pd, Pt, Ru or Cu. Particular preference is given to using catalysts based on Cu or Pd.
- SUMM Suitable heterogeneous catalyst systems generally comprise one of the aforementioned transition metal compounds on an inert support. Suitable inorganic supports are the customary oxides, especially silicas and aluminas, aluminosilicates, zeolites, carbides, nitrides, etc. and mixtures thereof. Preferred supports are Al.sub.2 O.sub.3, SiO.sub.2 and mixtures thereof. The heterogeneous catalysts used in the process of the invention are in particular those described in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are all fully incorporated herein by reference. Further suitable Cu-based catalyst systems are marketed by Dow Chemical as KLP catalyst.
- SUMM a) feeding the partly hydrogenated C.sub.4 cut, hydrogen cyanide and hydrocyanation catalyst into a reactor,
- SUMM e) working up the liquid and solid reactor effluent by distillation and

recycling the recovered catalyst into the reactor.

- SUMM The three components of the reaction mixture, hydrogen cyanide, partly hydrogenated C.sub.4 cut and catalyst, are generally fed in separate feeds at the rate of their respective consumption. If instead of a homogeneous catalyst, which can be introduced into the reactor for example separately as a solution in a suitable solvent or together with one of the other feeds, a heterogeneous catalyst is used, the latter can also be preinstalled in the reactor in a suitable form.
- SUMM The liquid and/or solid reactor effluent is subjected to a distillative workup to isolate the desired products 3-pentenitrile and 2-methyl-3-butenitrile and also to recover the catalyst present. The recovered active catalyst is recycled into the reactor.
- SUMM a) filling a pressure-resistant reactor with the partly hydrogenated C.sub.4 cut, hydrogen cyanide and a hydrocyanation catalyst and optionally a solvent,
- SUMM The pressure-resistant reactor is charged with the partly hydrogenated C.sub.4 cut, hydrogen cyanide, a hydrocyanation catalyst and optionally a solvent before commencement of the reaction. Examples of suitable solvents are aromatic hydrocarbons, such as toluene and xylene, or tetrahydrofuran.
- SUMM To complete the reaction, the reaction time can be followed by a postreaction time of from 0 minutes to about 5 hours, preferably from about 1 hour to 3 hours, during which no further hydrogen cyanide is introduced into the autoclave. The temperature during this period is left essentially constant at the previously set reaction temperature. The workup is carried out according to commonly used processes and comprises removing the unconverted 1,3-butadiene and the unconverted hydrogen cyanide, for example by washing or extraction and the distillative workup of the remaining reaction mixture to remove the products of value and recover still active catalyst.
- SUMM Suitable catalysts for the hydrocyanation are known from the prior art and include heterogeneous and preferably homogeneous catalyst systems. In general, catalysts suitable for the process of the invention are based on a transition metal of the 8th subgroup and optionally comprise a metal salt as promoter. The catalyst system used for the monoaddition of hydrogen cyanide preferably contains no addition of promoter.
- SUMM The process of the invention is preferably carried out using at least one homogeneous catalyst selected from salts or complexes of nickel. Of particular suitability are Ni(0) complexes with phosphine, phosphinite, phosphonite or preferably phosphite ligands. Suitable nickel phosphine, phosphinite, phosphonite or phosphite complexes have the general formula  $\text{NiL.sub.4}$ , where L is PR.sub.3, P(OR)R.sub.2, P(OR).sub.2 R or P(OR).sub.3 and R is alkyl, cycloalkyl or aryl, preferably phenyl or m,p-tolyl. It is also possible to use mixtures of different radicals R. In a preferred embodiment, the reaction takes place in the presence of an Ni(0) complex which comprises at least one multidentate phosphine, phosphinite, phosphonite or phosphite ligand. Suitable phosphite chelators are described in WO 96/22968, U.S. Pat. No. 5,484,902, WO 96/11182, U.S. Pat. No. 5,523,453, WO 95/30680, WO 95/28228 and WO 95/14659, which are all fully incorporated herein by reference.

- SUMM The aforementioned catalysts can be used combined with a promoter, if desired. The promoter used is preferably a Lewis acid, for example  $\text{AlCl}_3$  or  $\text{ZnCl}_2$ . The catalysts used for the monoaddition of hydrogen cyanide preferably contain no addition of a promoter.
- SUMM 2. Isomerization of the 2-methyl-3-butenitrile in these mixtures to 3-pentenitrile and isomerization of the resulting 3-pentenitrile and of the 3-pentenitrile already present in the mixtures from step 1 to form various n-pentenitriles. The proportion of 3-pentenitrile formed should be as high as possible and the proportion of conjugated, catalyst-poisoning 2-pentenitrile and 2-methyl-2-butenitrile should be as low as possible.
- SUMM The nickel phosphite catalysts preferred for the novel preparation of monoolefinic nitriles in step 1 are advantageously also suitable for the position and double bond isomerization in step 2 and the second addition of hydrogen cyanide in step 3. A suitable procedure involves for example the monoaddition of step 1 being carried out in the absence of promoters, for example Lewis acids such as  $\text{ZnCl}_2$ , the isomerization of step 2 being carried out in the presence of Lewis acids, to optimize the yield of 3-pentenitrile, and the second addition in step 3 being optionally carried out with the  $\text{ZnCl}_2$  having been replaced by triphenylboron to optimize the adiponitrile selectivity of the reaction.
- SUMM The industrially preferred continuous form of the process of the invention affords hydrogen cyanide conversions in the region of about 98% for untreated C.sub.4 cut under reaction conditions which are otherwise identical to those of the process of this invention compared with essentially complete conversions in the region of, for example, 99.8% on use of C.sub.4 cut pretreated according to the invention. Since the continuous process is carried out with recycling of the active nickel catalyst, and the catalyst is added to the reaction mixture only in small amounts, even a slight hydrogen cyanide excess due to incomplete conversion has a strongly adverse effect on the nickel balance of the reaction. Thus, the continuous process of the invention surprisingly has a higher catalyst recycling rate and so longer catalyst on-stream times than known processes. This is also relevant from ecological aspects, since the nickel cyanide formed from the active catalyst and hydrogen cyanide is highly toxic and has to be expensively worked up or disposed of.
- SUMM It is preferable to obtain a high proportion of 4-pentenitrile and also of products which are isomerizable to 4-pentenitrile, such as 3-pentenitrile and 2-methyl-3-butenitrile. Furthermore, the proportion of conjugated 2-pentenitrile, which acts as a catalyst poison, is low and is preferably below 1% by weight, especially within the range from about 0.1 to 0.2% by weight, based on C.sub.4 cut used.
- SUMM As gas space analyses show, if C.sub.4 cut is used for the hydrocyanation which has not been partly hydrogenated, it is not only 1,3-butadiene which is hydrocyanated, but also the alkynes and 1,2-dienes present, to form products having a C,C double bond conjugated with the nitrile function. Owing to the effect of these compounds as catalyst poisons, the nickel retrieval rates and the catalyst on-stream times are lower than in the process of the invention. Lower catalyst activities lead to lower conversions.
- SUMM The invention further provides a process for selective hydrogenation of C.sub.4 cuts, which comprises reacting a 1,3-butadiene-containing hydrocarbon mixture which additionally includes at least one alkyne

and/or 1,2-diene with hydrogen in the presence of a hydrogenation catalyst.

SUMM The present invention further provides a process for preparing adiponitrile, which comprises catalytically hydrocyanating a C.sub.5 mononitrile mixture prepared as described above, optionally after further workup or isomerization.

DETD Catalyst Composition

DETD Partly hydrogenated C.sub.4 cut, catalyst solution and hydrogen cyanide are introduced into a two stage stirred tank battery (pressure: 15 bar, temperature of reactor 1: 102° C., temperature of reactor 2: 95° C., residence time: 40 min/reactor). The effluent is stripped free from hydrocyanic acid and butadiene, the gas space is analyzed, and the gaseous effluent is passed through an NaOH scrubbing tower. Liquid/solid effluents are analyzed, worked up by distillation to remove the products of value and recover still active catalyst, and the products thus obtained are again analyzed. The HCN conversions are determined by volumetric analysis of the reactor solutions from the two reactors. The nickel retrieval rate (recovery of active catalyst) is determined by means of elemental analysis.

DETD An unhydrogenated hydrocarbon mixture of the above-specified composition is reacted similarly to Example 1, except that the catalyst feed is raised from 2.72 mmol/h to 4.85 mmol/h. The results are likewise reproduced in Table 1.

DETD As Example 1 and Comparative Examples 1 and 2 clearly show, the hydrogen cyanide conversion on using a selectively hydrogenated hydrocarbon mixture is higher than with an untreated mixture. Furthermore, Example 1 gives distinctly higher nickel retrieval rates than the comparative examples. The butadiene selectivity is about 1% higher in the process of the invention than in the reference process. Example 1 has less butadiene (excess component) than Comparative Examples 1 and 2. Nonetheless, the conversion of HCN (deficient component) is higher. This effect is surprising, because the conversion of the deficient component should have increased with increasing amount of excess component. Comparative Example 2, which utilizes a distinctly higher catalyst content, still does not match the results of Example 1.

DETD 4.7 g of catalyst composition containing:

DETD A glass autoclave is charged with 20.3 g of partially hydrogenated C.sub.4 cut (corresponding to 7.9 g (0.14 mol) of 1,3-butadiene), 2.75 g of a mixed catalyst (composition: 0.69 g (0.468 mmol) of tetrakis(tri-m/p-tolylphosphite)nickel(0), 1.65 g (4.68 mmol) of tri-m/p-tolylphosphite and 0.41 g 3-pentene nitrile) and 40 g of toluene at room temperature and heated to 90 ° C., the initial pressure being 4.4 bar. A mixture of 3.2 g (0.117 mol) of freshly distilled hydrogen cyanide in 40 g of toluene is continuously metered in over a period of 100 minutes, whereupon the pressure drops to 3.1 bar. The reaction is then completed by further reacting at 90° C. for another 120 minutes. The course of the reaction is monitored by pressure and temperature measurements. After cooling off, the liquid reaction product is analyzed.

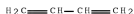
1. A process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, wherein the hydrocarbon mixture is reacted with hydrogen in the presence of a hydrogenation catalyst capable of hydrogenating alkynes and 1,2-dienes with high selectivity without significantly diminishing the 1,3-butadiene content in order to remove alkynes, 1,2-dienes and mixtures thereof partially or completely so that the proportion of those components in the hydrocarbon mixture which impair the catalytic

hydrocyanation is diminished and then subjecting the resulting mixture to catalytic hydrocyanation.

5. The process of claim 1, wherein the hydrocyanation catalyst catalyzes the position isomerization and double bond isomerization of the hydrocarbon mixture and/or of the nitriles as well as the hydrogen cyanide addition.

7. A process for preparing adiponitrile, which comprises catalytically hydrocyanating a C.sub.5 mononitrile mixture prepared as claimed in any of claims 1 to 6, optionally after further workup or isomerization.

IT 106-99-0, Butadiene, reactions  
(hydrocyanation in purified C4 fractions)  
IT 4635-87-4P, 3-Pentenitrile 16529-56-9P, 2-Methyl-3-butenitrile  
(monoolefinic C5 mononitrile production and use)  
IT 74-90-8, Hydrocyanic acid, reactions  
(reaction with butadiene)  
IT 106-99-0, Butadiene, reactions  
(hydrocyanation in purified C4 fractions)  
RN 106-99-0 USPATFULL  
CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenitrile  
(monoolefinic C5 mononitrile production and use)  
RN 4635-87-4 USPATFULL  
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8, Hydrocyanic acid, reactions  
(reaction with butadiene)  
RN 74-90-8 USPATFULL  
CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 58 OF 60 USPATFULL on STN  
ACCESSION NUMBER: 1999:1880 USPATFULL Full-text  
TITLE: Process for the hydrocyanation of organic compounds  
containing ethylenic unsaturation  
INVENTOR(S): Huser, Marc, Villeurbanne, France

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	NUMBER	KIND	DATE
PATENT INFORMATION:	US 5856555		19990105
APPLICATION INFO.:	US 1997-832689		19970411 (8)

	NUMBER	DATE
PRIORITY INFORMATION:	FR 1995-11689	19950929
	US 1996-15480P	19960412 (60)

DOCUMENT TYPE: Utility  
FILE SEGMENT: Granted  
PRIMARY EXAMINER: Richter, Johann  
ASSISTANT EXAMINER: Murray, Joseph  
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NUMBER OF CLAIMS: 21  
EXEMPLARY CLAIM: 1  
LINE COUNT: 932

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The present invention relates to a process for the hydrocyanation of organic compounds containing ethylenic unsaturation to nitrites, in particular the hydrocyanation of diolefins or of substituted olefins, such as alkenenitriles.

More specifically, it comprises a process for the hydrocyanation of organic compounds containing at least one ethylenic double bond by reaction with hydrogen cyanide in the presence of an aqueous solution of a catalyst comprising at least one transition metal compound and at least one water-soluble phosphine, characterized in that the said water-soluble phosphine is a monodentate or bidentate phosphine.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . alkylene radical, a cycloalkylene radical, an arylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or. . .

SUMM . . . diphenylene radical, a naphthylene radical, a dinaphthylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or. . .

SUMM . . . is possible, in practice, to charge to a reactor which has been purged beforehand using an inert gas (such as nitrogen or argon) either an aqueous solution containing all or part of the various constituents, such as the water-soluble phosphine, the transition metal. . .

SUMM It is possible, if appropriate, in this alternative form, to gently sweep the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which could still be present.

DETD . . . of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.

DETD . . . of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.



- DETD . . . of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD . . . of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD . . . of Ni(cyclooctadiene).sub.2, followed by 350 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- CLM What is claimed is:
- . . . carbon atoms, a phenylene radical, a diphenylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or . . .
  - . . . cycloalkylene radical, a phenylene radical, a diphenylene radical and a radical derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or . . .
- IT 74-30-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, 1,3-Butadiene, reactions 110-83-8, Cyclohexene, reactions 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, 4-Pentene nitrile 1319-73-9, Methylstyrene 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butene nitrile 4635-87-4, 3-Pentene nitrile 13284-42-9, 2-Pentene nitrile 16529-56-9, 2-Methyl-3-butene nitrile 26588-32-9, Vinyl naphthalene (process and water-soluble catalysts for the preparation of nitriles by the hydrocyanation of alkenes and cyanoalkenes)
- SUMM L represents a single valency bond or a divalent hydrocarbon radical, such as an alkylene radical, a cycloalkylene radical, an arylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally part of the divalent radical L to contain one or a number of substituents, such as an alkyl group having 1 to 4 carbon atoms.
- SUMM The preferred water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which Ar1 and Ar2 are phenyl groups or phenyl groups containing one or two substituents as defined above, Ar3 is a phenyl group containing one or two substituents as defined above, D is an alkyl group having from 1 to 6 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkyl group having from 1 to 6 carbon atoms containing one or a number of substituents as defined above or a cycloalkyl group having 5 to 8 carbon atoms containing one or a number of substituents as defined above and L is a single valency bond, an alkylene radical having from 1 to 6 carbon atoms, a monocyclic or bicyclic cycloalkylene radical having from 4 to 12 carbon atoms, a phenylene radical, a diphenylene radical, a naphthylene radical, a dinaphthylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally part of the divalent radical L to contain one or a number of substituents, such as an alkyl group having 1 to 4 carbon atoms.

- SUMM Within the context of a batchwise implementation, it is possible, in practice, to charge to a reactor which has been purged beforehand using an inert gas (such as nitrogen or argon) either an aqueous solution containing all or part of the various constituents, such as the water-soluble phosphine, the transition metal compound, the possible reducing agent and the possible solvent, or the said constituents separately. Generally, the reactor is then brought to the chosen temperature and then the pentenenitrile is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and uniformly.
- SUMM It is possible, if appropriate, in this alternative form, to gently sweep the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which could still be present.
- DETD 50 ml of a solution of 11.3 mmol of sodium salt of 1,2-bis[di(sulphonatophenyl)phosphinomethyl]-cyclobutane (CBDTNa.sub.4) in water are charged to a 100 ml round-bottomed glass flask equipped with a magnetic bar and an ascending reflux condenser; this solution is degassed. 2 g (7.3 mmol) of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD 50 ml of a solution of 32.8 mmol of sodium salt of tris(para-phosphophenyl)phosphine (TPPPNa.sub.6) in water are charged to a 100 ml round-bottomed glass flask equipped with a magnetic bar and an ascending reflux condenser; this solution is degassed. 2 g (7.3 mmol) of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD 50 ml of a solution of 32.8 mmol of sodium salt of bis(meta-sulphophenyl)(para-carboxyphenyl)-phosphine (DSPCPNa.sub.3) in water are charged to a 100 ml round-bottomed glass flask equipped with a magnetic bar and an ascending reflux condenser; this solution is degassed. 2 g (7.3 mmol) of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD 50 ml of a solution of 32.8 mmol of sodium salt of bis(meta-sulphophenyl)(2-sulphoethyl)phosphine (DSPSEPN.sub.3) in water are charged to a 100 ml round-bottomed glass flask equipped with a magnetic bar and an ascending reflux condenser; this solution is degassed. 2 g (7.3 mmol) of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD 500 ml of a solution of 300 mmol of sodium salt of tris(meta-sulphophenyl)phosphine (TPPTSNa.sub.3) in water are charged to a 1000 ml round-bottomed glass flask equipped with a stirrer and an ascending reflux condenser; this solution is degassed. 20 g (73 mmol) of Ni(cyclooctadiene).sub.2, followed by 350 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
2. The process according to claim 1, wherein the water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which Ar1 and Ar2 are phenyl groups or phenyl groups containing one or two substituents, Ar3 is a phenyl group containing one or two substituents, D is an alkyl group having from 1 to 6 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkyl group having from 1 to 6 carbon atoms containing one or a number of substituents or a cycloalkyl group having 5 to 8 carbon atoms containing one or a number of substituents

and L is a single valency bond, an alkylene radical having from 1 to 6 carbon atoms, a monocyclic or bicyclic cycloalkylene radical having from 4 to 12 carbon atoms, a phenylene radical, a diphenylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally part of the divalent radical L to contain one or a number of substituents.

21. The process of claim 1, wherein said water-soluble phosphine is a monodentate or bidentate phosphine corresponding to the general formula (II) in which L is a divalent hydrocarbon radical selected from the group consisting of an alkylene radical, a cycloalkylene radical, a phenylene radical, a diphenylene radical and a radical derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally part of the divalent radical L to contain one or a number of substituents.

- IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, 1,3-Butadiene, reactions 110-83-8, Cyclohexene, reactions 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, 4-Pentene nitrile 1319-73-9, Methylstyrene 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butene nitrile 4635-87-4, 3-Pentene nitrile 13284-42-9, 2-Pentene nitrile 16529-56-9, 2-Methyl-3-butene nitrile 26588-32-9, Vinylnaphthalene  
(process and water-soluble catalysts for the preparation of nitriles by the hydrocyanation of alkenes and cyanoalkenes)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions 4635-87-4, 3-Pentene nitrile  
(process and water-soluble catalysts for the preparation of nitriles by the hydrocyanation of alkenes and cyanoalkenes)
- RN 74-90-8 USPATFULL
- CN Hydrocyanic acid (CA INDEX NAME)



- RN 106-99-0 USPATFULL
- CN 1,3-Butadiene (CA INDEX NAME)



- RN 4635-87-4 USPATFULL
- CN 3-Pentenitrile (CA INDEX NAME)



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ACCESSION . . .

are converted to nitriles by reacting with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble therein; especially for making 3-pentene nitrile from butadiene.

CAS INDEXING IS AVAILABLE. . .

AB . . . are converted to nitriles by reacting with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble therein; especially for making 3-pentene nitrile from butadiene.

SUMM . . . nitriles and, more particularly, to their manufacture by reaction of olefinic compounds with hydrogen cyanide in the presence of a catalyst.

SUMM . . . nitriles which comprises reacting an olefin with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble in the said thiol or sulphide.

SUMM . . . unsaturation. Moreover, the heterocyclic rings containing the S atom may contain carbon-carbon unsaturation and may contain other hetero atoms, especially nitrogen, oxygen or sulphur atoms. Preferably the heterocyclic rings have 5, 6 or 7, especially 5 or 6, atoms in the. . .

SUMM . . . may be carried out over a wide range of temperatures, for example from -25° to 200°C. Because of decay of catalyst at higher temperatures, however, and because of the low rate of reaction at lower temperatures it preferred to operate in. . .

SUMM . . . range of olefin to hydrogen cyanide of 2 : 1 to 1 : 10. The cuprous salt is used in catalytic amount: this will normally fall within the range 0.0005 to 0.1 mole per mole of olefin. We prefer that the. . .

SUMM . . . hydrogen cyanide in the presence of, for example, cuprous chloride, to give 3-pentene nitrile. Although the reaction is described as catalytic good yields of 3-pentene nitrile are obtained only if substantially equimolar proportions of butadiene and cuprous salt are used. With catalytic proportions, for example 0.006 moles of cuprous chloride per mole of butadiene, both the conversion of butadiene and the yield of 3-pentene nitrile are low. In the process of our invention, however, catalytic amounts of cuprous salt, when used in conjunction with an organic thiol or sulphide, give good conversions of butadiene and. . .

SUMM It has already been proposed to react butadiene and hydrogen cyanide in the presence of catalytic amounts of certain catalysts, for example certain zerovalent nickel catalysts, as described, for example, in United Kingdom patent specification No. 1,104,140. Such processes give mixtures of linear pentene nitriles, which. . . is the ratio of 3-pentene nitrile to branched methyl butenenitriles is at least 4 : 1. Moreover, the zero-valent nickel catalysts used in the prior process are sensitive to moisture whereas the catalysts used in the process of our present invention are not. Thus, anhydrous conditions are not required and it is not. . .

SUMM 3-Pentene nitrile is particularly valuable for further reaction with hydrogen cyanide in the presence of a catalyst to give adiponitrile.

- Adiponitrile may be hydrogenated to hexamethylene diamine, a valuable intermediate for polycondensation with dicarboxylic acids to give. . .
- DETD . . . ml. of di-n-propyl sulphide (or the compound specified in the Table) and the solution introduced into a tube filled with nitrogen. After purging with nitrogen, 5 ml. of hydrogen cyanide, redistilled from phosphorus pentoxide, were condensed into the tube at -78°C. 10 ml. of butadiene, . . . cooled to -78°C and opened. Unreacted butadiene and hydrogen cyanide were distilled off and the remaining liquor filtered from solid catalyst. The liquor was then analysed by gas-liquid chromatography for 3-pentene nitrile 2-methyl-3-butene nitrile and adiponitrile.
- DETD Anhydrous cuprous chloride (0.6 g.) was dissolved in 1 ml. of di-n-propyl sulphide in a tube filled with nitrogen and 8.2 g. of isoprene were introduced. After purging with nitrogen, 5 ml. of hydrogen cyanide, distilled from phosphorus pentoxide, were introduced and the tube sealed. The mixture was then stirred. . .
- DETD . . . ml. of hydrogen cyanide, and heating was continued for 20 hours at 140°C, the liquid product was filtered from solid catalyst and distilled to give 4.93 g. of 4-methyl-3-pentenitrile, b.pt. 158°-162°C of greater than 97% purity. The conversion of isoprene was. . .
- IT 74-90-8 (addition reaction of, with butadiene and isoprene, catalysts for)
- IT 78-79-5, reactions 106-99-0, reactions (addition reaction of, with hydrocyanic acid, catalysts for)
- IT 4635-87-4P 16529-56-9P (from butadiene by reaction with hydrocyanic acid, catalysts for)
- PI US 3947487 19760330 <--
- AB Olefins are converted to nitriles by reacting with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble therein; especially for making 3-pentene nitrile from butadiene.
- SUMM This invention relates to the manufacture of organic nitriles and, more particularly, to their manufacture by reaction of olefinic compounds with hydrogen cyanide in the presence of a catalyst.
- SUMM Our invention provides a process for the manufacture of organic nitriles which comprises reacting an olefin with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble in the said thiol or sulphide.
- SUMM in which R.sub.1 and R.sub.2 are aliphatic, cycloaliphatic, araliphatic or aromatic radicals, and, in the case of sulphides, may be the same or different, and may be joined to form, with the S atom, a heterocyclic ring containing sulphur. The radicals R.sub.1 and R.sub.2 may carry substituents, for example hydroxyl, alkoxyl, carboxylic ester and halogen substituents, and the aliphatic and cycloaliphatic radicals they represent may contain carbon-carbon unsaturation, especially ethylene unsaturation. Moreover, the heterocyclic rings containing the S atom may contain carbon-carbon unsaturation and may contain other hetero atoms, especially nitrogen, oxygen or sulphur atoms. Preferably the heterocyclic rings have 5, 6 or 7, especially 5 or 6, atoms in the ring.
- SUMM The process of our invention may be carried out over a wide range of temperatures, for example from -25° to 200°C. Because of decay of catalyst at higher temperatures, however, and because of the low rate of reaction at lower temperatures it preferred to operate in the temperature range 50° to 160°C, and more preferably from 90° to 135°C, temperatures of about 120°C

being very suitable. Owing to the volatility and toxicity of hydrogen cyanide the reaction is preferably conducted in a closed vessel under autogenous pressure or, if desired, under deliberately raised pressure, for example at a pressure of from 1 to 50 atmospheres. If desired a solvent may be used, for example a hydrocarbon solvent such as benzene, toluene or xylene or a nitrile solvent such as acetonitrile, propionitrile, benzonitrile or adiponitrile. Agitation of the reactants is desirable. The reaction is continued for a time sufficient to give a suitable conversion. In the case of a batch process the time will normally be for from 1 hour up to a period of several days, for example 5 days.

SUMM The olefin and the hydrogen cyanide may be used in equimolar proportions or an excess of either may be used, especially within the molar range of olefin to hydrogen cyanide of 2 : 1 to 1 : 10. The cuprous salt is used in catalytic amount: this will normally fall within the range 0.0005 to 0.1 mole per mole of olefin. We prefer that the proportion of the said salt is from 0.005 to 0.05 mole per mole of olefine.

SUMM U.S. Pat. No. 2,509,859 describes the reaction of butadiene and hydrogen cyanide in the presence of, for example, cuprous chloride, to give 3-pentene nitrile. Although the reaction is described as catalytic good yields of 3-pentene nitrile are obtained only if substantially equimolar proportions of butadiene and cuprous salt are used. With catalytic proportions, for example 0.006 moles of cuprous chloride per mole of butadiene, both the conversion of butadiene and the yield of 3-pentene nitrile are low. In the process of our invention, however, catalytic amounts of cuprous salt, when used in conjunction with an organic thiol or sulphide, give good conversions of butadiene and good yields of 3-pentene nitrile.

SUMM It has already been proposed to react butadiene and hydrogen cyanide in the presence of catalytic amounts of certain catalysts, for example certain zerovalent nickel catalysts, as described, for example, in United Kingdom patent specification No. 1,104,140. Such processes give mixtures of linear pentene nitriles, which are convertible by further reaction with hydrogen cyanide into adiponitrile, and branched methyl butene nitriles which cannot be converted directly into adiponitrile. The proportion of linear pentene nitriles compared with branched methyl butene nitriles produced in such processes is not normally greatly in excess of 70% by weight (or molar). It is an advantage of the process of our invention that the proportion of linear 3-pentene nitrile, directly convertible to adiponitrile, which is produced is much higher, usually at least 80% by weight (or molar), that is the ratio of 3-pentene nitrile to branched methyl butenenitriles is at least 4 : 1. Moreover, the zero-valent nickel catalysts used in the prior process are sensitive to moisture whereas the catalysts used in the process of our present invention are not. Thus, anhydrous conditions are not required and it is not therefore necessary, for example, to specially dry the olefin and hydrogen cyanide.

SUMM 3-Pentene nitrile is particularly valuable for further reaction with hydrogen cyanide in the presence of a catalyst to give adiponitrile. Adiponitrile may be hydrogenated to hexamethylene diamine, a valuable intermediate for polycondensation with dicarboxylic acids to give polyamides, especially, for example, with adipic acid to give polyhexamethylene adipamide (nylon 6,6), a well-known polyamide for use in the manufacture of mouldings and for melt spinning into synthetic fibres.

- DETD Anhydrous cuprous chloride (0.6 g.) was dissolved in 0.9 ml. of di-n-propyl sulphide (or the compound specified in the Table) and the solution introduced into a tube filled with nitrogen. After purging with nitrogen, 5 ml. of hydrogen cyanide, redistilled from phosphorus pentoxide, were condensed into the tube at  $-78^{\circ}\text{C}$ . 10 ml. of butadiene, purified by passage through an ion exchange column, were then distilled into the tube which was then sealed. The mixture was then stirred magnetically and heated to the operating temperature for the operating period (see Table). The tube was then cooled to  $-78^{\circ}\text{C}$  and opened. Unreacted butadiene and hydrogen cyanide were distilled off and the remaining liquor filtered from solid catalyst. The liquor was then analysed by gas-liquid chromatography for 3-pentene nitrile 2-methyl-3-butene nitrile and adiponitrile.
- DETD Anhydrous cuprous chloride (0.6 g.) was dissolved in 1 ml. of di-n-propyl sulphide in a tube filled with nitrogen and 8.2 g. of isoprene were introduced. After purging with nitrogen, 5 ml. of hydrogen cyanide, distilled from phosphorus pentoxide, were introduced and the tube sealed. The mixture was then stirred magnetically and heated at  $110^{\circ}\text{C}$  for 17 hours. After cooling, the tube was opened, excess volatile material distilled off and the residue distilled to give 8.2 g. of mononitriles (71.7% conversion of isoprene), over 95% of which was 4-methyl-3-pentenitrile.
- DETD In an experiment conducted similarly to that in Example 4 except that the reactants were 0.6 g. of anhydrous cuprous chloride, 1 g. of dibenzyl sulphide, 8 g. of isoprene and 5 ml. of hydrogen cyanide, and heating was continued for 20 hours at  $140^{\circ}\text{C}$ , the liquid product was filtered from solid catalyst and distilled to give 4.93 g. of 4-methyl-3-pentenitrile, b.pt.  $158^{\circ}\text{--}162^{\circ}\text{C}$  of greater than 97% purity. The conversion of isoprene was 44.1%.
- IT 74-90-8  
(addition reaction of, with butadiene and isoprene, catalysts for)
- IT 78-79-5, reactions 106-99-0, reactions  
(addition reaction of, with hydrocyanic acid, catalysts for)
- IT 4635-87-4P 16529-56-9P  
(from butadiene by reaction with hydrocyanic acid, catalysts for)
- IT 74-90-8  
(addition reaction of, with butadiene and isoprene, catalysts for)
- RN 74-90-8 USPATFULL
- CN Hydrocyanic acid (CA INDEX NAME)



- IT 106-99-0, reactions  
(addition reaction of, with hydrocyanic acid, catalysts for)
- RN 106-99-0 USPATFULL
- CN 1,3-Butadiene (CA INDEX NAME)



- IT 4635-87-4P

(from butadiene by reaction with hydrocyanic acid, catalysts for)  
 RN 4635-87-4 USPATFULL  
 CN 3-Pentenitrile (CA INDEX NAME)



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ACCESSION . . .  
 THIS PATENT.

- AB Organic nitriles are obtained by reaction of an olefin and hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt, especially a cuprous halide and an organic acid. With butadiene as the olefin. . .
- AB Organic nitriles are obtained by reaction of an olefin and hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt, especially a cuprous halide and an organic acid. With butadiene as the olefin. . .
- SUMM . . . nitriles and, more particularly, to their manufacture by reaction of olefinic compounds with hydrogen cyanide in the presence of a catalyst.
- SUMM . . . Group IB of the Periodic System, for example cuprous chloride, to give 3-pentene nitrile. Although the reaction is described as catalytic good yields of 3-pentene nitrile are obtained only if substantially equimolar proportions of butadiene and Group IB metal halide are used. With catalytic proportions, for example 0.006 moles of cuprous chloride per mole of butadiene, both the conversion of butadiene and the yield. . .
- SUMM We have now found that good yields of product are obtained using only catalytic amounts of Group IB metal salt if the said salt is used in conjunction with an organic acid.
- SUMM . . . process for the manufacture of organic nitriles which comprises reacting an olefin with hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt and an organic acid.
- SUMM . . . normally be for from 1 hour up to a period of several days, for example 5 days. If a supported catalyst is used the time of contact could be as low as a few seconds, for example 3 seconds.
- SUMM . . . the molar range of olefin to hydrogen cyanide of 2:1 to 1:4. The Group IB metal salt is used in catalytic amount: this will normally fall within the range 0.0005 to 0.1 moles per mole of olefin. We prefer that the. . .
- SUMM . . . olefin and/or hydrogen cyanide by distillation or by simply venting the apparatus. The organic nitrile may then be separated from catalyst residues by conventional methods such as filtration with or without extraction with solvent, or by distillation. The process may readily. . .
- SUMM . . . Specification No. 2,509,859 the process of our invention enables the conversion to be effected in good yield using only a catalytic amount of Group IB metal halide, in conjunction with the organic acid instead of the equimolar amount required by the. . .
- SUMM 3-Pentene nitrile is particularly valuable for further reaction with hydrogen cyanide in the presence of a catalyst to give adiponitrile. Adiponitrile may be hydrogenated to hexamethylene diamine, a valuable intermediate for polycondensation with dicarboxylic acids to give. . .
- SUMM It has already been proposed to react butadiene and hydrogen cyanide in the presence of catalytic amounts of certain catalysts, for example certain zero valent nickel catalysts, as described, for example, in United Kingdom Specification No. 1,104,140. Such processes give mixtures



of linear pentene nitriles, which are. . . adiponitrile, which is produced is much higher, usually at least 80% by weight (or molar). Moreover, the zero valent nickel catalysts used in the prior process are sensitive to moisture whereas the catalysts used in our process are not. Thus, anhydrous conditions are not required and it is not, therefore, necessary, for example, . . .

CLM What is claimed is:

. . . molar ratio 2:1 to 1:4 at a temperature within the range -25° to 200°C in the presence, as a sole catalyst, of from 0.0005 to 0.1 moles per mole of butadiene of cuprous chloride, bromide or iodide and a carboxylic acid. . .

IT 4635-87-4P

(preparation of)

IT 74-90-8

(reaction of, with butadiene)

IT 106-99-0, reactions

(with hydrocyanic acid)

PI US 3869501 19750304 <--|

AB Organic nitriles are obtained by reaction of an olefin and hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt, especially a cuprous halide and an organic acid. With butadiene as the olefin the nitrile product contains more than 80% by weight of linear 3-pentene nitrile.

SUMM This invention relates to the manufacture of organic nitriles and, more particularly, to their manufacture by reaction of olefinic compounds with hydrogen cyanide in the presence of a catalyst.

SUMM United States Patent Specification No. 2,509,859 describes the reaction of butadiene and hydrogen cyanide in the presence of a halide of a metal of Group IB of the Periodic System, for example cuprous chloride, to give 3-pentene nitrile. Although the reaction is described as catalytic good yields of 3-pentene nitrile are obtained only if substantially equimolar proportions of butadiene and Group IB metal halide are used. With catalytic proportions, for example 0.006 moles of cuprous chloride per mole of butadiene, both the conversion of butadiene and the yield of 3-pentene nitrile are low.

SUMM We have now found that good yields of product are obtained using only catalytic amounts of Group IB metal salt if the said salt is used in conjunction with an organic acid.

SUMM Accordingly our invention provides a process for the manufacture of organic nitriles which comprises reacting an olefin with hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt and an organic acid.

SUMM The process of our invention may be carried out over a wide range of temperatures, for example from -25° to 200°C, preferably from 20° to 150°C, and more preferably from 50° to 120°C. Owing to the volatility and toxicity of hydrogen cyanide the reaction is preferably conducted in a closed vessel under autogenous pressure or, if desired, under deliberately raised pressure, for example at a pressure of from 1 to 50 atmospheres. If desired a solvent may be used, for example a hydrocarbon solvent such as benzene, toluene or xylene or a nitrile solvent such as acetonitrile, propionitrile, benzonitrile or adiponitrile. Agitation of the reactants is desirable. The reaction is continued for a time sufficient to give a suitable conversion. In the case of a batch process the time will normally be for from 1 hour up to a period of several days, for example 5 days. If a supported catalyst is used the time of contact could be as low as a

few seconds, for example 3 seconds.

SUMM The olefin and the hydrogen cyanide may be used in equimolar proportions or an excess of either may be used, especially within the molar range of olefin to hydrogen cyanide of 2:1 to 1:4. The Group IB metal salt is used in catalytic amount: this will normally fall within the range 0.0005 to 0.1 moles per mole of olefin. We prefer that the proportion of the said salt is from 0.005 to 0.05 moles per mole of olefin.

SUMM The organic nitrile formed in the process may be separated from the reaction mixture by first removing any excess olefin and/or hydrogen cyanide by distillation or by simply venting the apparatus. The organic nitrile may then be separated from catalyst residues by conventional methods such as filtration with or without extraction with solvent, or by distillation. The process may readily be adapted to continuous operation.

SUMM The process of our invention is particularly valuable for the conversion of butadiene to 3-pentene nitrile. Compared with the process of United States Patent Specification No. 2,509,859 the process of our invention enables the conversion to be effected in good yield using only a catalytic amount of Group IB metal halide, in conjunction with the organic acid instead of the equimolar amount required by the prior process.

SUMM 3-Pentene nitrile is particularly valuable for further reaction with hydrogen cyanide in the presence of a catalyst to give adiponitrile. Adiponitrile may be hydrogenated to hexamethylene diamine, a valuable intermediate for polycondensation with dicarboxylic acids to give polyamides, especially, for example, with adipic acid to give polyhexamethylene adipamide (nylon 6,6), a well-known polyamide for use in the manufacture of mouldings and for melt spinning into synthetic fibres.

SUMM It has already been proposed to react butadiene and hydrogen cyanide in the presence of catalytic amounts of certain catalysts, for example certain zero valent nickel catalysts, as described, for example, in United Kingdom Specification No. 1,104,140. Such processes give mixtures of linear pentene nitriles, which are convertible by further reaction with hydrogen cyanide into adiponitrile, and branched methylbutene nitriles which cannot be converted directly to adiponitrile. The proportion of linear pentene nitriles compared with branched methylbutene nitriles produced in such processes is not normally greatly in excess of 70% by weight (or molar). It is an advantage of the process for our invention that the proportion of linear 3-pentene nitrile, directly convertible to adiponitrile, which is produced is much higher, usually at least 80% by weight (or molar). Moreover, the zero valent nickel catalysts used in the prior process are sensitive to moisture whereas the catalysts used in our process are not. Thus, anhydrous conditions are not required and it is not, therefore, necessary, for example, to specially dry the olefin and hydrogen cyanide.

1. A process for the manufacture of 3-pentene nitrile which comprises reacting butadiene with hydrogen cyanide in the molar ratio 2:1 to 1:4 at a temperature within the range  $-25^{\circ}$  to  $200^{\circ}\text{C}$  in the presence, as a sole catalyst, of from 0.0005 to 0.1 moles per mole of butadiene of cuprous chloride, bromide or iodide and a carboxylic acid selected from benzoic acid, oxalic acid and compounds having one or two carboxylic acid groups attached to a saturated or ethylenically unsaturated hydrocarbon residue containing up to three carbon atoms and

10/586490

IT 4635-87-4P  
(preparation of)  
IT 74-90-8  
(reaction of, with butadiene)  
IT 106-99-0, reactions  
(with hydrocyanic acid)  
IT 4635-87-4P  
(preparation of)  
RN 4635-87-4 USPATFULL  
CN 3-Pentenitrile (CA INDEX NAME)



IT 74-90-8  
(reaction of, with butadiene)  
RN 74-90-8 USPATFULL  
CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions  
(with hydrocyanic acid)  
RN 106-99-0 USPATFULL  
CN 1,3-Butadiene (CA INDEX NAME)



=&gt; d his full

(FILE 'HOME' ENTERED AT 14:42:47 ON 01 FEB 2008)

FILE 'ZCAPLUS' ENTERED AT 14:43:01 ON 01 FEB 2008

FILE 'CAPLUS' ENTERED AT 14:43:07 ON 01 FEB 2008

E US2006-586490/APPS

L1 1 SEA ABB=ON PLU=ON US2006-586490/AP  
D SCA

FILE 'REGISTRY' ENTERED AT 14:44:22 ON 01 FEB 2008

L2 1 SEA ABB=ON PLU=ON 4635-87-4  
L3 1 SEA ABB=ON PLU=ON 16529-56-9  
L4 1 SEA ABB=ON PLU=ON 74-90-8  
L5 1 SEA ABB=ON PLU=ON 106-99-0  
D SCA  
D SCA L3  
D SCA L2

L6 2248 SEA ABB=ON PLU=ON PENTENENITRILE/CNS  
L7 136 SEA ABB=ON PLU=ON L6 AND 5/C  
L8 64 SEA ABB=ON PLU=ON L7 AND STEREOSEARCH/FS  
E 3-PENTENENITRILE, (3E)-/CN  
L9 2 SEA ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN  
D SCA L2  
L10 3 SEA ABB=ON PLU=ON L2 OR L9  
SEL RN  
L11 2 SEA ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1/CRN OR  
4635-87-4/CRN)  
D SCA

L12 465 SEA ABB=ON PLU=ON 3-PENTENENITRILE/CNS  
L13 5 SEA ABB=ON PLU=ON L10 OR L11  
L14 460 SEA ABB=ON PLU=ON L12 NOT L13  
L15 432 SEA ABB=ON PLU=ON L14 AND NC<2  
L16 34 SEA ABB=ON PLU=ON L15 AND 5/C  
D SCA  
E "3-PENTENENITRILE-2,2-D2 "/CN  
E "3-PENTENENITRILE-2,2-D2"/CN

L17 1 SEA ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN  
L18 6 SEA ABB=ON PLU=ON L13 OR L17  
D SCA  
L19 1 SEA ABB=ON PLU=ON L18 AND NC>2  
D SCA

FILE 'ZCAPLUS' ENTERED AT 14:56:54 ON 01 FEB 2008

FILE 'CAPLUS' ENTERED AT 14:56:59 ON 01 FEB 2008

L\*\*\* DEL 830 S L19  
L20 0 SEA ABB=ON PLU=ON L19

FILE 'REGISTRY' ENTERED AT 14:57:20 ON 01 FEB 2008

D LC L19

FILE 'CAPLUS' ENTERED AT 14:57:21 ON 01 FEB 2008

FILE 'REGISTRY' ENTERED AT 14:57:44 ON 01 FEB 2008

D ED L19

FILE 'CAPLUS' ENTERED AT 14:57:44 ON 01 FEB 2008

FILE 'REGISTRY' ENTERED AT 14:58:09 ON 01 FEB 2008

D SCA L3

D SCA L4

D SCA L5

FILE 'CAPLUS' ENTERED AT 14:58:30 ON 01 FEB 2008

L21 17208 SEA ABB=ON PLU=ON L4  
 L22 24982 SEA ABB=ON PLU=ON L5  
 L23 383 SEA ABB=ON PLU=ON L18  
 L24 47 SEA ABB=ON PLU=ON L21 AND L22 AND L23  
 L25 130 SEA ABB=ON PLU=ON L18 (L) PREP/RL  
 L26 3070185 SEA ABB=ON PLU=ON (RACT OR RCT OR RGT)/RL  
 L27 2588 SEA ABB=ON PLU=ON L21 (L) L26  
 L28 9152 SEA ABB=ON PLU=ON L22 (L) L26  
 L29 32 SEA ABB=ON PLU=ON L27 AND L28 AND L25  
 L30 297092 SEA ABB=ON PLU=ON ?POROUS?/BI  
 L31 40403 SEA ABB=ON PLU=ON MICROPOR?/BI  
 E MOLECULAR SIEVES+ALL/CT  
 L32 30953 SEA ABB=ON PLU=ON MOLECULAR SIEV?/BI  
 L33 128603 SEA ABB=ON PLU=ON ZEOLIT?/BI  
 L34 23369 SEA ABB=ON PLU=ON MESOPOR?/BI  
 L35 1378 SEA ABB=ON PLU=ON ADSORBANT?/BI  
 L36 375297 SEA ABB=ON PLU=ON CERAMIC?/BI  
 L37 54059 SEA ABB=ON PLU=ON AIR/CT  
 E NOBLE GASES+ALL/CT  
 L38 18350 SEA ABB=ON PLU=ON NOBLE GAS?/BI  
 L39 15276 SEA ABB=ON PLU=ON HELIUM GROUP?/BI  
 L40 1 SEA ABB=ON PLU=ON L29 AND (L30 OR L31 OR L32 OR L33 OR L34  
 OR L35 OR L36)  
 D SCA  
 L41 1 SEA ABB=ON PLU=ON L29 AND (L37 OR L38 OR L39)  
 D SCA  
 L42 2 SEA ABB=ON PLU=ON L24 AND (L30 OR L31 OR L32 OR L33 OR L34  
 OR L35 OR L36 OR L37 OR L38 OR L39)  
 D SCA

FILE 'USPATFULL' ENTERED AT 15:09:13 ON 01 FEB 2008

L43 24 SEA ABB=ON PLU=ON L4 AND L5 AND L18  
 L44 6 SEA ABB=ON PLU=ON L43 AND (L30 OR L31 OR L32 OR L33 OR L34  
 OR L35 OR L36)  
 L45 2 SEA ABB=ON PLU=ON L43 AND (L37 OR L38 OR L39)  
 L46 1 SEA ABB=ON PLU=ON L44 AND L45  
 L47 250630 SEA ABB=ON PLU=ON HELIUM OR ARGON OR NEON OR KRYPTON OR  
 XENON OR RADON  
 L48 14 SEA ABB=ON PLU=ON L47 AND L43  
 D KWIC 1-4  
 L49 4 SEA ABB=ON PLU=ON L44 AND L47  
 L50 1664593 SEA ABB=ON PLU=ON AIR OR NITROGEN  
 L51 15 SEA ABB=ON PLU=ON L43 AND L50  
 L52 19 SEA ABB=ON PLU=ON L48 OR L51  
 L53 485246 SEA ABB=ON PLU=ON CATALY?  
 L54 24 SEA ABB=ON PLU=ON L43 AND L53

FILE 'CAPLUS' ENTERED AT 15:13:52 ON 01 FEB 2008

L55 TRA PLU=ON L25 1- PN : 646 TERMS

FILE 'USPATFULL' ENTERED AT 15:13:59 ON 01 FEB 2008

L56 56 SEA ABB=ON PLU=ON L55

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L57 18 SEA ABB=ON PLU=ON L56 AND L54  
L58 1664602 SEA ABB=ON PLU=ON L44 OR L45 OR L48 OR L50 OR L57  
L59 24 SEA ABB=ON PLU=ON L44 OR L45 OR L48 OR L51 OR L57

FILE 'CAPLUS' ENTERED AT 15:15:58 ON 01 FEB 2008

L60 FILE 'REGISTRY' ENTERED AT 15:16:33 ON 01 FEB 2008  
1 SEA ABB=ON PLU=ON 1344-28-1  
D SCA

L61 FILE 'CAPLUS' ENTERED AT 15:16:46 ON 01 FEB 2008  
4 SEA ABB=ON PLU=ON L60 AND L24  
E ALUMINA/CT  
E ALUMINA+ALL/CT  
L62 314410 SEA ABB=ON PLU=ON ALUMINA/BI  
L63 4 SEA ABB=ON PLU=ON L24 AND L62  
L64 1462878 SEA ABB=ON PLU=ON ?CATALY?/BI  
L65 43 SEA ABB=ON PLU=ON L64 AND L24  
L66 32 SEA ABB=ON PLU=ON L64 AND L29  
L67 33 SEA ABB=ON PLU=ON L40 OR L41 OR L42 OR L61 OR L63 OR L66

L68 FILE 'CASREACT' ENTERED AT 15:20:52 ON 01 FEB 2008  
39 SEA ABB=ON PLU=ON L18/PRO  
D QUE L4  
L69 723 SEA ABB=ON PLU=ON 74-90-8  
D QUE L5  
L70 1995 SEA ABB=ON PLU=ON 106-99-0  
L71 16 SEA ABB=ON PLU=ON L68 (L) L69  
L72 15 SEA ABB=ON PLU=ON L71 (L) L70  
D SCA

L73 FILE 'CAPLUS' ENTERED AT 15:24:40 ON 01 FEB 2008  
15 SEA ABB=ON PLU=ON L72  
L74 12 SEA ABB=ON PLU=ON L73 AND L24  
L75 3 SEA ABB=ON PLU=ON L73 NOT L74  
D SCA  
SEL AN

L76 FILE 'REGISTRY' ENTERED AT 15:29:29 ON 01 FEB 2008  
1 SEA ABB=ON PLU=ON NITROGEN/CN  
L77 1 SEA ABB=ON PLU=ON HELIUM/CN  
L78 1 SEA ABB=ON PLU=ON ARGON/CN  
L79 1 SEA ABB=ON PLU=ON KRYPTON/CN  
L80 1 SEA ABB=ON PLU=ON NEON/CN  
L81 1 SEA ABB=ON PLU=ON XENON/CN  
L82 1 SEA ABB=ON PLU=ON RADON/CN  
L83 1 SEA ABB=ON PLU=ON AIR/CN  
L\*\*\* DEL 0 S L24 AND L76-L83

L84 FILE 'CAPLUS' ENTERED AT 15:31:03 ON 01 FEB 2008  
2 SEA ABB=ON PLU=ON L24 AND (L76 OR L77 OR L78 OR L79 OR L80  
OR L81 OR L82 OR L83)  
L85 0 SEA ABB=ON PLU=ON L75 AND (L76 OR L77 OR L78 OR L79 OR L80  
OR L81 OR L82 OR L83)

FILE 'REGISTRY' ENTERED AT 15:32:42 ON 01 FEB 2008

FILE 'CAPLUS' ENTERED AT 15:32:45 ON 01 FEB 2008  
D STAT QUE L40  
D STAT QUE L41

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      D STAT QUE L42
      D STAT QUE L61
      D STAT QUE L63
      D STAT QUE L66
      D STAT QUE L84
L86      34 SEA ABB=ON  PLU=ON  L40 OR L41 OR L42 OR L61 OR L63 OR L66 OR
      L84

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FILE 'CASREACT' ENTERED AT 15:33:41 ON 01 FEB 2008
      D STAT QUE L72

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FILE 'USPATFULL' ENTERED AT 15:34:03 ON 01 FEB 2008
      D STAT QUE L44
      D STAT QUE L45
      D STAT QUE L48
      D STAT QUE L51
      D STAT QUE L57
L87      24 SEA ABB=ON  PLU=ON  L44 OR L45 OR L48 OR L51 OR L57

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FILE 'STNGUIDE' ENTERED AT 15:35:01 ON 01 FEB 2008

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FILE 'CAPLUS, CASREACT, USPATFULL' ENTERED AT 15:35:24 ON 01 FEB 2008
L88      60 DUP REM L86 L72 L87 (13 DUPLICATES REMOVED)
      ANSWERS '1-34' FROM FILE CAPLUS
      ANSWERS '35-37' FROM FILE CASREACT
      ANSWERS '38-60' FROM FILE USPATFULL
      D IBIB ABS HITIND HITSTR L88 1-34
      D IBIB ABS HIT L88 35-37
      D IBIB ABS KWIC HIT HITSTR L88 38-60

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FILE HOME

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FILE ZCAPLUS

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FILE COVERS 1907 - 1 Feb 2008  VOL 148 ISS 6
FILE LAST UPDATED: 31 Jan 2008  (20080131/ED)

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FILE CAPLUS

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DICTIONARY FILE UPDATES: 31 JAN 2008 HIGHEST RN 1001228-41-6

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#### FILE USPATFULL

FILE COVERS 1971 TO PATENT PUBLICATION DATE: 31 Jan 2008 (20080131/PD)  
FILE LAST UPDATED: 31 Jan 2008 (20080131/ED)  
HIGHEST GRANTED PATENT NUMBER: US7325253  
HIGHEST APPLICATION PUBLICATION NUMBER: US2008028492  
CA INDEXING IS CURRENT THROUGH 31 Jan 2008 (20080131/UPCA)  
ISSUE CLASS FIELDS (/INCL) CURRENT THROUGH: 31 Jan 2008 (20080131/PD)  
REVISED CLASS FIELDS (/NCL) LAST RELOADED: Dec 2007  
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Dec 2007

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FILE CONTENT:1840 - 26 Jan 2008 VOL 148 ISS 5

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FILE STNGUIDE

FILE CONTAINS CURRENT INFORMATION.

LAST RELOADED: Jan 25, 2008 (20080125/UP).

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